
Hypersonic-Flow Governing Equations with Electromagnetic Fields

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Abstract

The paper deals with the formulation of a consistent set of governing equations apt to describe the physical phenomenology comprising the hypersonic flow field of an ionized gas mixture and the electromagnetic field. The governing equations of the flow field and those of the electromagnetic field are revisited in sequence and differences or similarities with past treatments are pointed out and discussed. The equations governing the flow field hinge on the customary balance of masses, momenta and energies. The equations governing the electromagnetic field are introduced both directly in terms of the Maxwell equations and by recourse to the scalar and vector potentials. The theory of linear irreversible thermodynamics based on the entropy-balance equation is also revisited for the purpose of obtaining, consistently with the presence of the electromagnetic field, the phenomenological relations required to bring the governing equations into a mathematically closed form. Old problems, such as the influence of the medium compressibility on chemical-relaxation rates or the importance of cross effects among generalized fluxes and forces, are re-discussed; additional problems, such as the necessity to consider the tensorial nature of the transport properties because of the presence of the magnetic field, are pointed out. A non-conventional choice of first-tensorial-order generalized forces and corresponding fluxes is proposed which appears to offer more simplicity and better convenience from a conceptual point of view when compared to alternative definitions customarily used in the literature. The applicability domain of the present formulation is clearly outlined and recommendations for further work are given.

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Nomenclature

A	vector potential
\mathcal{A}_k	affinity of k -th chemical reaction
B	magnetic induction
C	constant (in Arrhenius law)
c	speed of light in vacuum, $299792458 \text{ m}\cdot\text{s}^{-1}$
\mathbf{D}_{ij}	diffusion tensor
\mathbf{D}_i^T	thermodiffusion tensor
\mathcal{D}_{ik}	diffusion tensor (Fick law)
\mathbf{d}_j	diffusion vector (kinetic theory)
E	electric-field intensity
E_a	activation energy (in Arrhenius law)
e	electronic charge, $1.602176462 \cdot 10^{-19} \text{ C}$
e_m	matter energy per unit total mass
$\dot{e}_{m,v}$	matter-energy production
$\dot{e}_{em,v}$	electromagnetic-energy production
\mathbf{F}_i	external force (kinetic theory)
\mathcal{F}_i	generalized force [Eq. (127)]
$f_{i\delta}$	Helmholtz potential of δ -th molecular degree of freedom of i -th component
G	generic extensive variable
g	generic-variable density (mass)
g_v	generic-variable density (volume)
\dot{g}	generic-variable production (mass)
\dot{g}_v	generic-variable production (volume)
h_i	enthalpy of i -th component per its unit mass
\mathbf{J}_G	generic-variable diffusive flux
\mathbf{J}_{E_m}	matter-energy diffusive flux
\mathbf{J}_{m_i}	component-mass diffusive flux
$\mathbf{J}_{m_j^*}$	element-mass diffusive flux
\mathbf{J}_Q	electric-charge diffusive flux or conduction-current density
\mathbf{J}_q	heat flux (see text)
\mathbf{J}_U	internal-energy diffusive flux
$\mathbf{J}_{U_{i\delta}}$	diffusive flux of $U_{i\delta}$ (see below)
\mathbf{J}_s	entropy diffusive flux
j	electric-current density
K_B	Boltzmann constant, $1.3806503 \cdot 10^{-23} \text{ J}\cdot\text{K}^{-1}$
K_k^c	chemical-equilibrium constant (concentrations)
ℓ_i	number of molecular degrees of freedom of i -th component
M	magnetization
M	gas-mixture average molar mass
M_i	component molar mass
M_j^a	element molar mass

n	number of components
N_A	Avogadro number, $6.02214199 \cdot 10^{23}$
\mathcal{N}_i	component particle number
\mathcal{N}_j^a	element particle number
P	polarization
p	pressure
p_i	partial pressure of i -th component
Q_i	component molar electric charge
q	electric charge per unit mass
R_G	universal gas constant, $8.314472 \text{ J}\cdot\text{K}^{-1}$
r	number of chemical reactions
s	number of elements
\mathcal{S}	entropy per unit total mass
\mathcal{S}_i	entropy of i -th component per its unit mass
$\dot{\mathcal{S}}_v$	entropy production
$\dot{\mathcal{S}}_{v,0,1,2}$	entropy production related to tensorial order 0, 1, 2
T	temperature (thermal equilibrium)
$T_{i\delta}$	temperature associated with δ -th molecular degree of freedom of i -th component
t	time
U	unit tensor
U	internal energy of the gas mixture
$U_{i\delta}$	internal energy distributed over δ -th molecular degree of freedom of i -th component
u	internal energy per unit total mass
$u_{i\delta}$	internal energy distributed over δ -th molecular degree of freedom of i -th component per unit mass of i -th component
\dot{u}_v	internal-energy production
$\dot{u}_{v,i\delta}$	production of $U_{i\delta}$
v	velocity vector
$(\nabla \mathbf{v})_o^s$	traceless symmetric part of velocity gradient
$(\nabla \mathbf{v})^a$	antisymmetric part of velocity gradient
v	specific volume
v_i	specific volume of i -th component
\dot{v}_v	volume production
\mathbf{w}_i	component diffusion velocity
x_i	molar fraction of i -th component
α_i	component mass fraction
α_j^a	element mass fraction
ε_0	dielectric constant of vacuum, $8.854187817 \cdot 10^{-12} \text{ F}\cdot\text{m}^{-1}$
η	temperature exponent (in Arrhenius law)
κ_k^f, κ_k^b	reaction constant (forward, backward)
λ_e	scalar electrical conductivity
λ_e	electrical-conductivity tensor

λ_{ej}^p	pressoelectrical-conductivity tensor
λ_e^T	thermoelectrical-conductivity tensor
λ'	thermal-conductivity tensor (see text)
μ_i	chemical potential of i -th component
μ	dynamic-viscosity tensor
μ_v	bulk-viscosity coefficient
ν_{ki}	global stoichiometric coefficient
$\nu_{ki}^{(r)}, \nu_{ki}^{(p)}$	stoichiometric coefficient (reactant, product)
$\dot{\xi}_k$	chemical-reaction rate
π	normal mean stress
ρ	total-mass density
ρ_c	electric-charge density
ρ_i	component partial density
ρ_j^a	element partial density
σ_{ij}	formation-matrix coefficient
τ	stress tensor
τ_o^s	traceless symmetric part of stress tensor
τ_M	Maxwell stress tensor
Φ_G	generic-variable flux
ϕ	scalar potential
\mathcal{X}_i	generalized force [Eq. (111)]

1 Introduction

Interest in theoretical investigations [1–26] aimed at the understanding of the fluid dynamics and the thermodynamics of flows subjected to the action of electric and/or magnetic fields can be traced back, at least, to the first half of the past century. The main driving motivation that justifies such an interest was probably best expressed by Resler and Sears [9] in 1958:

If a fluid is a conductor of electricity, the possibility arises that an *electric body force* may be produced in it that will affect the fluid flow pattern in a significant way ... The attractive thing about the electric body force ... is that it can be controlled, insofar as the current and the magnetic field can be controlled, and perhaps made to serve useful purposes such as acceleration or deceleration of flow, prevention of separation, and the like.

Since those pioneering years, the scientific/engineering discipline in question has been going through a continuous process of maturation. This process, however, has been continuously and systematically marked in time by researchers' complaints about the unsatisfactory state-of-the-art of the theory. Indeed, notwithstanding many efforts, and the voluminous literature generated by them, to confer the discipline the status of being firmly established on physically rigorous and consistent foundations freed from *ad hoc* assumptions, progress to achieve convergence to that goal appears today not completed yet.

The study presented here was carried out in the context of a research activity motivated by renewed interest in investigating the influence that electric and/or magnetic fields can exert on the thermal loads imposed on a body invested by a hypersonic flow [18,27–34]. In this regard, spacecraft thermal protection during planetary (re)entry represents the driving engineering application. The contents of the study should be considered, to a certain extent, a systematic reexamination of past work complemented with somewhat innovative ideas. The aim concentrates on the formulation of a consistent set of governing equations in open form apt to describe the physical phenomenology comprising the hypersonic flow field of an ionized gas mixture and the presence of the electromagnetic field. The discourse opens with stoichiometric considerations that are important to comprehend how specific parameters of electromagnetic nature, namely electric-charge density and conduction-current density, can be expressed in terms of variables of fluid-dynamics nature. Subsequently, the governing equations of the flow field and those of the electromagnetic field are revisited in sequence; differences or similarities with past treatments are pointed out and discussed. The equations governing the flow field hinge on the customary balance of masses, momenta and energies. The equations governing the electromagnetic field are introduced both directly in terms of the Maxwell equations and by recourse to the scalar and vector potentials. In the latter case, the convenience of adopting the Lorentz gauge, rather than the magnetosta-

tic gauge, in order to obtain field equations with favorable mathematical symmetry is adequately pointed out. Features, limitations and approximations implied in the open-form governing equations are explicitly addressed. Thermodynamics aspects associated with the necessity to assign the thermodynamic model of the gas mixture are described and discussed. The theory of linear irreversible thermodynamics [20,21,23,35–37] based on the entropy-balance equation is examined for the purpose of obtaining, consistently with the presence of the electromagnetic field, the phenomenological relations required to bring into a mathematically closed form the governing equations. Old problems, such as the influence of medium compressibility on chemical-reaction rates or the importance of cross effects among generalized fluxes and forces, are re-discussed; additional problems, such as the necessity to take into account the tensorial nature of the transport properties because of the anisotropy introduced by the magnetic field, are pointed out. A non-conventional choice of first-tensorial-order generalized forces and corresponding fluxes is proposed which appears to offer more simplicity and better convenience from a conceptual point of view when compared to alternative definitions customarily used in the literature.

Polarization and magnetization have not been considered in this study. Setting aside their expected negligibility in hypersonic flows, there is an important reason behind that choice. The inclusion of polarization and magnetization effects in the Maxwell equations is conceptually (almost) straightforward. That, however, would constitute only a unilateral approach to the physical phenomenology. Indeed, the important fact should not be overlooked on the fluid-dynamics side that not only body-force distributions but also torque distributions exist [21,38] within a polarized and magnetized medium subjected to the action of the electromagnetic field. Under these circumstances, the velocity vector is not the sole kinematic unknown that characterizes the flow field; the specific angular momentum [21,23,38] of matter may not identically vanish throughout the flow field, as it usually happens in the absence of polarization and magnetization, and must necessarily be taken into account as an additional kinematic unknown. The appearance of the corresponding balance equation in the set of the governing equations is inescapable. A non-vanishing specific angular momentum in matter can have far reaching consequences. For example, the stress tensor loses its symmetry; its antisymmetric part, conjointly with the antisymmetric part of the velocity-vector gradient, contributes to produce entropy and the familiar Newton law does not suffice anymore to characterize the tensional state in the medium. Implications of energetic nature should also be expected because there is energy associated with specific angular momentum; in addition, the polarization and magnetization vectors belong to the set of the thermodynamic independent state parameters [19,20]. These and similar aspects cannot be ignored at the moment of constructing a physically rigorous theory, even if the mentioned effects may turn out to be negligible under specific flow circumstances. The complexity of the physical phenomenology in the presence of polarization and magnetization increases enormously and its study presupposes a degree of difficulty which can be adequately tackled only after that acquisition of solid understanding of the coupling

between fluid dynamics and pure electromagnetic field has been secured. The latter constitutes the main target of the present study and the motivation to postpone to future investigations the behaviour of polarized and magnetized media.

2 Stoichiometric aspects

The chemical constituents that compose an ionized gas mixture can be subdivided in neutral components, ionized components and free electrons. The knowledge of how many and which components intervene within a given flow problem relies on experimental evidence complemented with the judicious choice dictated by the researcher's expertise. The acquisition of such knowledge is sometimes straightforward, sometimes rather involved; in any case, it constitutes a problem of its own. When the n components are identified then it is possible to recognize the s ($s \leq n$) *reference elements* that participate in their formation. There is, obviously, a certain arbitrariness in the qualification of the reference elements. For example, either the molecule N₂ can be considered formed by putting together two N atoms or, vice versa, the atom N can be considered formed by breaking the N₂ molecule; the role of reference element is played by N or N₂ in the former or latter case, respectively. For reasons of convenience, the reference elements are enumerated in such a way that the first ($s - 1$) are the true atoms/molecules E^1, E^2, \dots, E^{s-1} and the last one E^s is the electron 'e' responsible for building the electric charge carried by the ionized components (if any). The formation concept is formalized in the chemical formula $E_{\sigma_{i1}}^1 E_{\sigma_{i2}}^2 \dots E_{\sigma_{is}}^s$ of the generic component. The coefficient σ_{ij} represents the number of E^j atoms/molecules required to form the i -th chemical component; if $\sigma_{ij} = 0$ then the j -th element does not intervene in the formation of the i -th component and the corresponding symbol (E^j) is dropped from the chemical formula. The non-vanishing coefficients σ_{ij} ($j = 1, \dots, s - 1$) are necessarily positive, even integers if the elements are monatomic. For a neutral component, the coefficient σ_{is} is identically zero. For an ionized component, the coefficient σ_{is} is positive or negative for exceeding or missing electrons and its opposite gives the electric charge carried by the component molecule as an integer multiple of the electronic charge. In a more common formalism, $E_{\sigma_{is}}^s$ is replaced by superscripting the chemical formula with '+' signs, if $\sigma_{is} < 0$, or '-' signs, if $\sigma_{is} > 0$, in number equal to $|\sigma_{is}|$. The coefficients σ_{ij} can be grouped together to compose the $(n \times s)$ formation matrix. The rightmost column ($j = s$) of the matrix is the electric-charge column which appears and acquires significance exclusively when ionized components are present in the mixture. The coefficients σ_{ij} permit to express the molar masses M_i of the components as linear combinations

$$M_i = \sum_{j=1}^s \sigma_{ij} M_j^* \quad (1)$$

of the molar masses M_j^* of the elements ($M_s^* = 5.48579911 \cdot 10^{-7}$ kg is the mass of one mole of electrons) intervening in their formation. The molar electric charges Q_i require only the coefficients in the electric-charge column

$$Q_i = -\sigma_{is} e N_A \quad (2)$$

in combination with the electronic charge $e = 1.602176462 \cdot 10^{-19}$ C and the Avogadro number $N_A = 6.02214199 \cdot 10^{23}$. An explicit example of formation matrix relative to a seven-component high-temperature air mixture reads

	N	O	e		N	N_2	O_2	e
N	1	0	0			1/2	0	0
O	0	1	0			0	1/2	0
e^-	0	0	1	or		0	0	1
NO	1	1	0		NO	1/2	1/2	0
N_2	2	0	0		N_2	1	0	0
O_2	0	2	0		O_2	0	1	0
NO^+	1	1	-1		NO^+	1/2	1/2	-1

depending whether atoms or molecules are chosen as reference elements. In this case, there are $n = 7$ components formed by $s = 3$ elements.

Another important construct is the stoichiometric matrix connected with the r chemical reactions

$$\sum_{i=1}^n \nu_{ki}^{(r)} [CF]_i \rightleftharpoons \sum_{i=1}^n \nu_{ki}^{(p)} [CF]_i \quad k = 1, 2, \dots, r \quad (3)$$

that can occur in the gas mixture; $\nu_{ki}^{(r)}, \nu_{ki}^{(p)}$ are the stoichiometric coefficients of reactants and products, respectively. The processes formalized in Eq. (3) are subjected to component-mass conservation

$$\sum_{i=1}^n \nu_{ki}^{(r)} M_i = \sum_{i=1}^n \nu_{ki}^{(p)} M_i \quad (4)$$

After defining the global stoichiometric coefficients $\nu_{ki} = \nu_{ki}^{(p)} - \nu_{ki}^{(r)}$, Eq. (4) can be recast into the form

$$\sum_{i=1}^n \nu_{ki} M_i = 0 \quad (5)$$

The coefficients ν_{ki} are integer numbers and are conveniently assembled in a $(r \times n)$ stoichiometric matrix. The combination of the formation concept embodied in Eq. (1) and the component-mass conservation enforced by Eq. (5) allows to obtain important conditions to which formation and stoichiometric matrices are subjected and that express physically the element-mass conservation. The substitution of Eq. (1) into Eq. (5) and the permutation of the sum operators yields

$$\sum_{j=1}^s M_j^* \sum_{i=1}^n \nu_{ki} \sigma_{ij} = 0 \quad (6)$$

Given the (mathematical) arbitrariness of the molar masses M_j^* , the solution

$$\sum_{i=1}^n \nu_{ki} \sigma_{ij} = 0 \quad (7)$$

is the sole possibility left to have Eq. (6) identically satisfied. It is interesting to notice that when $j = s$, and taking in account Eq. (2), Eq. (7) yields the electric-charge conservation

$$\sum_{i=1}^n \nu_{ki} Q_i = 0 \quad (8)$$

across the given chemical reaction. The conservation of the electric charge is, therefore, not an independent statement but follows from the mass conservation relative to the *electron* as reference element.

The formation matrix permits to express composition parameters, and their properties, related to the elements in terms of those related to the components. The basic relation, in this regard, is the one that connects particle number of the elements with particle number of the components

$$\mathcal{N}_j^* = \sum_{i=1}^n \mathcal{N}_i \sigma_{ij} \quad (9)$$

From Eq. (9), for example, one obtains similar expressions for mass fractions

$$\alpha_j^* = \sum_{i=1}^n \frac{\alpha_i}{M_i} \sigma_{ij} M_j^* \quad (10)$$

and partial densities

$$\rho_j^* = \sum_{i=1}^n \frac{\rho_i}{M_i} \sigma_{ij} M_j^* \quad (11)$$

The electric charge per unit mass also follows from Eq. (9) after setting $j = s$ and multiplying by $-e$; it reads

$$q = -eN_A \frac{\alpha_s^*}{M_s^*} = -eN_A \sum_{i=1}^n \frac{\alpha_i}{M_i} \sigma_{is} \quad (12)$$

In turn, multiplication of Eq. (12) by the total-mass density ρ provides the expression for the electric-charge density

$$\rho_c = \rho q = -eN_A \frac{\rho_s^*}{M_s^*} = -eN_A \sum_{i=1}^n \frac{\rho_i}{M_i} \sigma_{is} \quad (13)$$

Equation (13) is an important relation. It establishes a first necessary link between the electromagnetic side (ρ_c) of the physical phenomenology and its fluid-dynamics counterpart (ρ_s^* or all ρ_i). It also endorses the idea that the electric-charge density should not be looked at as a basic field unknown because it can be straightforwardly calculated when the gas mixture composition has been determined.

3 Physical significance of the balance equations

In view of the analysis in the following sections, it appears appropriate to dwell preliminarily upon an important aspect related to the physical significance of the balance equations which becomes manifest when the presence of the electromagnetic field has to be considered.

It is a recurrent occurrence in the mechanics of continuous media that important equations governing the dynamic evolution of a system, namely the portion of the medium contained in a specified control volume, are developed from the idea of balancing the variations of the extensive properties (mass, momentum, energy, etc) that characterize the macroscopic state of the system. If G is any generic extensive variable owned by the system and g_v , Φ_G , \dot{g}_v are respectively its density, flux and production, then the typical balance equation

$$\frac{\partial g_v}{\partial t} = -\nabla \cdot \Phi_G + \dot{g}_v \quad (14)$$

is the translation in mathematical language of the basic principle [35,36,39] affirming that the variable G can vary in time t only for two specific reasons: a) an exchange with the external environment and b) an internal production. Equation (14) constitutes the local formulation of such a principle and establishes a formal link between time variation and reasons of change. Density and production in Eq. (14) carry the subscript v to emphasize that they are referred to unit volume. Feynman

provided a very interesting disquisition in his famous lectures [40] concerning the physics behind Eq. (14); his reasoning, although expounded in didactic style, is certainly one of the most lucid accounts the present author ever had the opportunity to read.

The aspect related to Eq. (14) that is meant to be pointed out here regards the possibility for the quantities g_v , Φ_G and \dot{g}_v of being attached directly to space instead of being associated with the matter occupying that same space. Such an occurrence is somewhat *forgotten* in traditional fluid dynamics because the physical variables are all associated with matter in that case. Indeed, customary practice proceeds one step further from Eq. (14) by introducing density $g = g_v/\rho$ and production $\dot{g} = \dot{g}_v/\rho$ referred to unit mass and by separating the flux

$$\Phi_G = \rho \mathbf{v} g + \mathbf{J}_G \quad (15)$$

in a convective part, associated with the flow velocity \mathbf{v} , that takes care of the transport associated with the macroscopic motion of matter and a diffusive part \mathbf{J}_G which takes care of everything else. Accordingly, Eq. (14) becomes

$$\frac{\partial \rho g}{\partial t} + \nabla \cdot (\rho \mathbf{v} g) = -\nabla \cdot \mathbf{J}_G + \rho \dot{g} \quad (16)$$

Equation (16) is the stencil that embeds all the governing equations belonging to traditional fluid dynamics. It comes to no surprise, therefore, that the mathematical structure of Eq. (16) has stood as the starting point in computational fluid dynamics (CFD) from which all efforts towards the development of numerical algorithms have originated. In this sense, Eq. (16) has undoubtedly contributed to forging the way of thinking in the CFD community. Yet, things may be looked at from a different perspective in the presence of the electromagnetic field. Obviously, the applicability of the convection-diffusion separation [Eq. (15)], pertaining to the flux Φ_G , and of Eq. (16) still survives when the fluid-dynamics field and the electromagnetic field have to coexist. However, Eq. (14) can also play a role if the definition of global variables, namely momentum and energy, are adequately generalized in a manner that relaxes the unnecessary conceptual habit of matter association; then the ensuing equations become statements of conservation ($\dot{g}_v = 0$) and, in so doing, they assume a mathematical structure that, in principle, may favorably lend itself to a more simplified numerical analysis.

In the following sections, the formal balance-equation concept will be explicated in relation to the fundamental physical quantities mass, momentum and energy in order to formulate a consistent set of governing equations. Concerning the latter two quantities, the programme will be carried out in a comparative fashion by confronting the fluid-dynamics habitual approach with the novel perspective just discussed and brought to surface by the presence of the electromagnetic field.

4 Mass-balance equations

The standard equations balancing the component masses

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}) = -\nabla \cdot \mathbf{J}_{m_i} + \sum_{k=1}^r \dot{\xi}_k \nu_{ki} M_i \quad i = 1, \dots, n \quad (17)$$

are available for the determination of the gas-mixture composition. The component-mass diffusive fluxes \mathbf{J}_{m_i} and the chemical-reaction rates $\dot{\xi}_k$ require the assignment of phenomenological relations (Secs. 8 and 9). Other variables with same requirement will be encountered in the sequel; they should be viewed as *windows* through which models, describing the physical behaviour of the medium, manifest their influence on the open-form governing equations. The component-mass diffusive fluxes are linked to the corresponding diffusion velocities

$$\mathbf{J}_{m_i} = \rho_i \mathbf{w}_i \quad (18)$$

and are subjected to the condition

$$\sum_{i=1}^n \mathbf{J}_{m_i} = \sum_{i=1}^n \rho_i \mathbf{w}_i = 0 \quad (19)$$

Equation (19) enforces the physical fact that total mass cannot diffuse. In other words, there are only $n - 1$ independent diffusive fluxes or diffusion velocities. Taking into account Eq. (5), Eq. (19) and mass additivity

$$\rho = \sum_{i=1}^n \rho_i \quad (20)$$

the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (21)$$

follows from the summation of Eq. (17) on the subscript i . There are two options for the determination of the $n + 1$ unknowns ρ_i, ρ . The most straightforward way would seem to consist in the selection of Eqs. (17) and (20) because the use a very simple algebraic equation, as Eq. (20) is, is appealing, of course. There is, however, a risk in doing so because potential inconsistencies carried into Eq. (17) by phenomenological relations for component-mass diffusive fluxes and chemical-reaction rates would produce inaccurate partial densities which, in turn, would pass on their inaccuracy to the total-mass density via Eq. (20). The alternative way to

proceed could be to replace Eq. (20) with Eq. (21). In this manner, the effect of the previously mentioned inconsistencies is somewhat contained because neither partial densities nor phenomenological relations are explicitly required in Eq. (21). As a matter of fact, Eq. (20) could be used aside, once the unknowns ρ_i, ρ have been obtained, as a sort of error verifier. The drawback of this approach consists in the necessity to solve an additional differential equation [Eq. (21)].

The chemical-reaction rates are known to be numerically stiff properties to deal with. It is, therefore, desirable to make them appear as sparingly as possible in the governing equations. To this aim, simplification can be achieved to some extent if the element-composition parameters are brought into the picture. Taking into account the definition of element partial densities [Eq. (11)], the balance equations of the element masses are obtained by multiplying Eq. (17) by $\sigma_{ij} M_j^* / M_i$ and summing on the subscript i ; they read

$$\frac{\partial \rho_j^*}{\partial t} + \nabla \cdot (\rho_j^* \mathbf{v}) = -\nabla \cdot \mathbf{J}_{m_j^*} \quad j = 1, \dots, s \quad (22)$$

The element-mass diffusive flux on the right-hand side of Eq. (22) turns out to be expressed in terms of the component-mass diffusive fluxes as

$$\mathbf{J}_{m_j^*} = \sum_{i=1}^n \frac{1}{M_i} \mathbf{J}_{m_i} \sigma_{ij} M_j^* \quad (23)$$

The production term is absent in Eq. (22) because Eq. (7) makes it vanish identically. Thus, the element masses are conservative: they cannot be either created or destroyed, regardless of the reactive mechanisms at work in the gas mixture. This occurrence suggests an advantageous manoeuvre to limit the appearance of the chemical-reaction rates. The idea is to relinquish as unknowns the last s partial densities ρ_i and replace them with the partial densities ρ_j^* ; at the same time, the last s equations of the set (17) are replaced with the set (22). In this way, the number of differential equations is unchanged but the chemical-reaction rates appear only in $n - s$ equations. The s relinquished partial densities ρ_i can be expressed in terms of the first $n - s$ partial densities ρ_i and of the s partial densities ρ_j^* from Eq. (11) after expanding

$$\rho_j^* = \sum_{i=1}^{n-s} \frac{\rho_i}{M_i} \sigma_{ij} M_j^* + \sum_{i=n-s+1}^n \frac{\rho_i}{M_i} \sigma_{ij} M_j^* \quad j = 1, \dots, s \quad (24)$$

and re-arranging

$$\sum_{i=n-s+1}^n \frac{\rho_i}{M_i} \sigma_{ij} M_j^* = \rho_j^* - \sum_{i=1}^{n-s} \frac{\rho_i}{M_i} \sigma_{ij} M_j^* \quad j = 1, \dots, s \quad (25)$$

Equation (25) represents an algebraic system of s equations for the s relinquished partial densities ρ_i . It can be formally solved in the following manner. First, introduce for brevity the $(s \times s)$ coefficient matrix

$$\hat{\sigma}_{ij} = \sigma_{ij} \frac{M_j^*}{M_i} \quad i = n-s+1, \dots, n; j = 1, \dots, s \quad (26)$$

and the $(1 \times s)$ known-term array

$$\hat{\rho}_j^* = \rho_j^* - \sum_{i=1}^{n-s} \frac{\rho_i}{M_i} \sigma_{ij} M_j^* \quad j = 1, \dots, s \quad (27)$$

so that Eq. (25) can be recast in the standard form

$$\sum_{i=n-s+1}^n \rho_i \hat{\sigma}_{ij} = \hat{\rho}_j^* \quad j = 1, \dots, s \quad (28)$$

The matrix $\hat{\sigma}_{ij}$ can be inverted once and forever when the formation matrix σ_{ij} and the element molar masses are known. Then, the formal solution of Eq. (28) is

$$\rho_i = \sum_{j=1}^s \hat{\rho}_j^* \hat{\sigma}_{ji}^{-1} \quad i = n-s+1, \dots, n \quad (29)$$

Another important aspect to look at in connection with the elements is the balancing of the electric charge. The electric-charge balance equation is not an independent statement but is embedded in Eq. (22) when particularized to the case of the electron element. Indeed, setting $j = s$ in Eq. (22) and multiplying it by $-eN_A/M_s^*$ [see Eq. (13)] yields the fluid-dynamics styled equation

$$\frac{\partial \rho_c}{\partial t} + \nabla \cdot (\rho_c \mathbf{v}) = -\nabla \cdot \mathbf{J}_Q \quad (30)$$

in which, taking into account Eq. (23) with $j = s$, the electric-charge diffusive flux turns out to be expressed by the following linear combination

$$\mathbf{J}_Q = -eN_A \mathbf{J}_{m_s^*} \frac{1}{M_s^*} = -eN_A \sum_{i=1}^n \frac{1}{M_i} \mathbf{J}_{m_i} \sigma_{is} \quad (31)$$

of the component-mass diffusive fluxes of the electrically charged components ($\sigma_{is} \neq 0$). It is important to notice that Eqs. (30) and (31) warn against any presumptive imposition of charge neutrality ($\rho_c = 0$) throughout the flow field; even

if there are zones in which the gas mixture is electrically neutral, the mass diffusion of ionized components and free electrons works towards the removal of such a condition. Rephrasing Eq. (30) in electromagnetic-theory style

$$\frac{\partial \rho_c}{\partial t} + \nabla \cdot (\rho_c \mathbf{v} + \mathbf{J}_Q) = 0 \quad (32)$$

leads to the identification of, in the corresponding parlance, the electric-current density

$$\mathbf{j} = \rho_c \mathbf{v} + \mathbf{J}_Q \quad (33)$$

and to the recognition of its separability in convection-current ($\rho_c \mathbf{v}$) and conduction-current (\mathbf{J}_Q) densities. These are the sole contributions that need to be accounted for in the absence of polarization and magnetization. Equation (31) represents the other important relation that establishes a second, and final, necessary link between electromagnetism (\mathbf{J}_Q) and fluid dynamics (all \mathbf{J}_{m_i}). Both Eq. (13) and Eq. (31) converge into the definition provided by Eq. (33) and, in so doing, enforce the unambiguous assertion that the electric-current density is specified entirely in terms of variables of fluid-dynamics nature. Also, the dependence expressed in Eq. (31) clearly shows that it is not necessary to pursue an independent phenomenological relation for the conduction-current density because the latter descends naturally from the knowledge of the phenomenological relations for the component-mass diffusive fluxes. It will be seen in Sec. 9.4 how the famous Ohm law and additional effects of thermodynamic origin arise naturally in this way.

5 Electromagnetic-field equations

The essence of electromagnetism finds its deepest representation in the differential equations that govern the electromagnetic field, namely the well known Maxwell equations. The body of didactic literature on this subject matter is enormous and the theory can very well be considered consolidated on solid foundations. The contents of this section take advantage mainly from Feynman's lectures [40]; Maxwell's fundamental treatise [41,42] together with the textbooks written by Møller [43], Lorrain and Colson [44], Persico [45], Tolman [46], and Pauli [47] were also helpful. Notwithstanding the satisfactory state-of-the-art of the theory, there is one peculiar aspect of electromagnetism that always deserves extreme care and attention: the choice of the physical units. In SI units, the Maxwell equations read

$$\nabla \cdot \mathbf{E} = \frac{\rho_c}{\epsilon_0} \quad (34)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (35)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (36)$$

$$\varepsilon_0 c^2 \nabla \times \mathbf{B} = \mathbf{j} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (37)$$

The electric-charge and electric-current densities represent the *channels* through which the coupling between fluid-dynamics field and electromagnetic field becomes manifest [recall Eq. (13), Eq. (31) and Eq. (33)]. The constants c and ε_0 are respectively the velocity of light ($299792458 \text{ m}\cdot\text{s}^{-1}$) in and the dielectric constant ($8.854187817 \cdot 10^{-12} \text{ F}\cdot\text{m}^{-1}$) of vacuum. In principle, Eqs. (36) and (37) are all that is required to associate with the fluid-dynamics equations in order to determine simultaneously electric-field intensity \mathbf{E} and magnetic induction \mathbf{B} . However, their mathematical structure is substantially distinct from the habitual fluid-dynamics stencil [Eq. (16)]. A widespread practice [34,48–55] that aims to derive and use an equation with more CFD-suitable form is based on the adaptation of Eq. (36) following the neglect of the displacement-current density ($\varepsilon_0 \partial \mathbf{E} / \partial t$) in Eq. (37) and the assumed validity of the generalized Ohm law

$$\mathbf{J}_Q = \lambda_e (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (38)$$

although with a scalar electrical conductivity λ_e . The method leads to an algebraic relation for the electric field

$$\mathbf{E} = \frac{\varepsilon_0 c^2}{\lambda_e} \nabla \times \mathbf{B} - \frac{\rho_c}{\lambda_e} \mathbf{v} - \mathbf{v} \times \mathbf{B} \quad (39)$$

and to the so-called magnetic-induction equation

$$\begin{aligned} \frac{\partial \mathbf{B}}{\partial t} + \nabla \cdot (\mathbf{v} \mathbf{B}) &= \nabla \cdot (\mathbf{B} \mathbf{v}) + \frac{\varepsilon_0 c^2}{\lambda_e} \nabla^2 \mathbf{B} + \frac{\varepsilon_0 c^2}{\lambda_e^2} \nabla \lambda_e \times (\nabla \times \mathbf{B}) \\ &+ \frac{\rho_c}{\lambda_e} \nabla \times \mathbf{v} - \mathbf{v} \times \nabla \left(\frac{\rho_c}{\lambda_e} \right) \end{aligned} \quad (40)$$

The details of the derivation of Eq. (40) are given in appendix A. Further simplified forms in the event of electric-charge neutrality ($\rho_c \simeq 0$) or uniform electrical conductivity ($\lambda_e \simeq \text{const}$) are easily deduced. Equation (40) looks certainly attractive from a numerical point of view because its structure reflects perfectly that of Eq. (16). In this way, the solution of the electromagnetic field is brought within the reach of familiar algorithms in CFD. At the same time, the idea of magnetic-field *convection* is favoured to find its way into the picture of the physical phenomenology. The computational fluid dynamicist is most likely satisfied with this situation because he is provided with an additional instrument [Eq. (40)] which features the same mathematical characteristics of familiar tools, namely the flow-field equations without the electromagnetic field. He can, then, proceed to calculate. Seen

from the perspective of the hard efforts and time invested in the development of numerical schemes, this attitude is comprehensible. Yet, the theoretical fluid dynamicist would feel concerned about the same situation because Eq. (40) and its associated interpretation are very much in contrast with the physical fact that the electromagnetic field is attached to space regardless of the matter flowing through that same space. In this regard, he may ponder about the physical significance of Eq. (40), asking important questions such as: can the vector \mathbf{B} be interpreted as the volume density of some extensive property of the matter moving in the space occupied by the electromagnetic field? If there is such a property then can the diadic tensor \mathbf{Bv} and the remaining terms on the right-hand side of Eq. (40) be interpreted as, respectively, its diffusive flux and production? The difficulty in finding convincing answers suggests a critical scrutiny of the assumptions on which Eq. (40) is built. The neglect of the displacement-current density is justifiable in circumstances of not rapidly varying electric field but it is still an undesirable limitation *at the moment of constructing a general theory*. The generalized Ohm law [Eq. (38)] is more prone to criticism. Concern about its applicability is not a novelty and was explicitly raised long time ago by Maxwell [41,42] and emphasized in more recent times by Napolitano [11,16], Pai [18] and Sedov [21]. The major hurdle to accept is the fact that the applicability of Eq. (40), which is a governing equation, is subjugated to the validity of Eq. (38), which is a phenomenological relation. This levies a serious toll on the generality of the ensuing theory because the latter becomes medium-dependent. Equation (17), for example, is medium-independent because it remains applicable regardless of the phenomenological relations assumed for the component-mass diffusive fluxes and chemical-reaction rates. This is not the case for Eq. (40). What happens if the tensorial nature of the electrical conductivity, a feature already discussed by Maxwell in 1873, cannot be neglected or, worst, if the medium does not comply with Eq. (38)? Indeed, and just to mention an example, Ohm law [Eq. (38)] becomes meaningless for a polarizable and magnetizable neutral gas. There can be no electrical conduction ($\mathbf{J}_Q = 0$) in such a gas because *free* electric charges are absent; yet there is an electrical-current density

$$\mathbf{j} = \frac{\partial \mathbf{P}}{\partial t} + \nabla \times \mathbf{M} \quad (41)$$

produced by the polarization \mathbf{P} and magnetization \mathbf{M} of the gas. In this case, the whole edifice built on the magnetic-induction equation [Eq. (40)] must be thrown away because absolutely inapplicable and a new theory must be constructed afresh. These arguments may appear irrelevant to the computational fluid dynamicist who is interested mainly in numerical algorithms but for the theoretical fluid dynamicist they are strong reasons of concern that originate from the awareness of operating on the basis of a theory whose solidity may be compromised in unforeseeable and uncontrollable particular situations.

Another exploitable method takes advantage of the scalar and vector potentials ϕ, \mathbf{A} often used in electromagnetism. The knowledge of the potentials implies that

of electric-field intensity and magnetic induction because the latter vectors follow from the definitions

$$\mathbf{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t} \quad (42)$$

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (43)$$

The substitution of Eqs. (42) and (43) into Eqs. (36) and (37) leads to the following nicely symmetrical field equations

$$\frac{1}{c^2} \frac{\partial^2\phi}{\partial t^2} = \nabla^2\phi + \frac{\rho_c}{\varepsilon_0} \quad (44)$$

$$\frac{1}{c^2} \frac{\partial^2\mathbf{A}}{\partial t^2} = \nabla^2\mathbf{A} + \frac{1}{\varepsilon_0 c^2} \mathbf{j} \quad (45)$$

The details of the derivation are provided in appendix B. The mathematical symmetry of Eqs. (44) and (45) is strongly dependent on the adoption of the condition

$$\frac{1}{c^2} \frac{\partial\phi}{\partial t} + \nabla \cdot \mathbf{A} = 0 \quad (46)$$

known as Lorentz gauge [40,47]. A similar approach was already pursued by Burgers [14] and Pai [18] who, however, opted for the typical magnetostatic gauge

$$\nabla \cdot \mathbf{A} = 0 \quad (47)$$

Instead of Eqs. (44) and (45), they obtained two much more complicated highly cross-coupled field equations in which terms involving ϕ and \mathbf{A} appear simultaneously in both equations.

Equations (44) and (45) indicate explicitly the wave-like evolution taking place in the electromagnetic field and how that is influenced by the presence of matter through the electric-charge and electric-current densities. The equations reduce to the Poisson equation in steady-state circumstances. It may be asked what is the gain of using Eqs. (44) and (45) rather than Eqs. (36) and (37) or Eq. (40). First of all, Eqs. (44) and (45) are four scalar differential equations instead of the six represented by Eqs. (36) and (37). Moreover, they are general and independent of the medium in so far as they are unaffected by arguments related to importance or disregard of the displacement-current density and as they need no appeal to any phenomenological relation to provide reason for their existence. It is true that, once again, Eqs. (44) and (45) do not reflect the structure of Eq. (16) and, therefore, they presuppose the necessity to develop new numerical algorithms for their simultaneous solution with the fluid-dynamics equations. On the other hand, they are

equations of the mathematical physics which have been studied numerically since long time and for whose properties a huge body of knowledge and understanding has been accumulated.

6 Momentum-balance equations

The determination of the velocity-vector field occurs via the equation balancing the momentum associated with the matter flowing in the control volume. For reasons that will appear evident soon, it is appropriate to emphasize the association to matter by systematically referring to this quantity with the term *matter momentum*. In the presence of the electromagnetic field, its balance equation assumes the form

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \boldsymbol{\tau} + \rho_c \mathbf{E} + \mathbf{j} \times \mathbf{B} \quad (48)$$

As in traditional fluid dynamics, the matter-momentum diffusion is characterized by the stress tensor $\boldsymbol{\tau}$ which requires the assignment of a phenomenological relation and, as anticipated in Sec. 1, preserves its feature of being a symmetrical tensor in the absence of polarization and magnetization. The gravitational contribution to the body force on the right-hand side of Eq. (48) has been omitted for compatibility with the typical circumstances settling in in hypersonic regime that presuppose the negligibility of gravitational effects with respect to those due to the tensional state of the medium. As a matter of fact, the inclusion in the discourse of a (Newtonian) gravitational field is conceptually straightforward because the gravitational body-force term can be treated similarly to the electric counterpart ($\rho_c \mathbf{E}$) and made fit smoothly in the equation framework described in the sequel. On the other hand, the emphasis of the present context addresses the importance of the electromagnetic field; the presence of a gravitational field would only burden the equations with unnecessary additional terms whose inclusion would not change at all the considerations that will follow and the conclusions that will be drawn.

The electromagnetic field produces matter momentum through the body force

$$\dot{\mathbf{g}}_v = \rho_c \mathbf{E} + \mathbf{j} \times \mathbf{B} \quad (49)$$

This is the term to which the statement of Resler and Sears [9] quoted in the introduction refers to and that is responsible for a variety of new effects substantially unimaginable in traditional fluid dynamics. Under the action of the electromagnetic field, for example, the mass diffusion of the electrically charged components takes an active role in affecting the motion of the fluid particles because it enters explicitly into the equation of their motion [Eq. (48)] via the electric-current density [see Eqs. (31) and (33)]. Without the electromagnetic field, mass diffusion produces

only an indirect effect on the dynamics of the flow field through a thermodynamic pathway that involves the gas-mixture composition and, subsequently, the pressure distribution; the latter, in turn, represents a substantial contribution to the build-up of the stress tensor.

Equation (48) is a necessary and sufficient equation qualified for inclusion in the governing set; one could be satisfied with its availability. Nevertheless, there are more interesting features of the physical phenomenology that await to be unravelled. Whether it may, perhaps, appear a somewhat fortuitous circumstance or it could be looked at as the manifestation of something of deep physical significance, it is certainly interesting that the Maxwell equations [Eqs. (34) and (37)] allow a very useful transformation [43,45–47] of the electromagnetic body force (49). In a single stroke, this transformation provides evidence of the existence of momentum associated with the electromagnetic field, namely the *electromagnetic momentum*, and leads to the formulation of its balance equation. The mathematical details are given in appendix C. The final outcome from the mentioned transformation provides the electromagnetic body force in the form

$$\rho_c \mathbf{E} + \mathbf{j} \times \mathbf{B} = \nabla \cdot \boldsymbol{\tau}_M - \frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) \quad (50)$$

In Eq. (50), the tensor $\boldsymbol{\tau}_M$ represents the following combination

$$\boldsymbol{\tau}_M = \varepsilon_0 (\mathbf{E}\mathbf{E} - \frac{1}{2} E^2 \mathbf{U}) + \varepsilon_0 c^2 (\mathbf{B}\mathbf{B} - \frac{1}{2} B^2 \mathbf{U}) \quad (51)$$

of electric-field intensity, magnetic induction and unit tensor \mathbf{U} . It is, therefore, a symmetric tensor. Equation (50) can be simply overturned as

$$\frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) = \nabla \cdot \boldsymbol{\tau}_M - (\rho_c \mathbf{E} + \mathbf{j} \times \mathbf{B}) \quad (52)$$

to match exactly the structure of Eq. (14). Hence, Eq. (52) is a balance equation. It shows unequivocally the existence of electromagnetic momentum distributed in space with density $\varepsilon_0 \mathbf{E} \times \mathbf{B}$ and transported through space with flux $-\boldsymbol{\tau}_M$. The symmetric tensor $\boldsymbol{\tau}_M$ plays in Eq. (52) the same role fulfilled by the stress tensor in Eq. (48) and, for this reason, it is suggestively named as *Maxwell stress tensor*. Equation (52) highlights in an evident manner also that the transport of electromagnetic momentum takes place through space exclusively in consequence of the presence of the electromagnetic field and bears no relation whatsoever with the matter transported through that same space. It is important to keep in mind that, although very useful, Eq. (52) is not a new independent equation. In principle, it can replace one of Eqs. (36) and (37) but it does not say anything more that is not already contained in the Maxwell equations. The nice features of Eq. (52) consist in its balance-equation structure and that it fulfills the task of permitting a deep

insight towards the understanding of the existence of important properties of the electromagnetic field that are not immediately recognizable from the equations of electromagnetism as given by Maxwell.

Another aspect worth of attention is that all the electromagnetic momentum that disappears locally turns out to reappear as matter momentum or viceversa. This is the obvious conclusion ensuing from the appearance of the electromagnetic body force both in Eq. (48) and, with changed sign, in Eq. (52). In other words, the sum of the two forms of momentum cannot be produced, either created or destroyed. Thus, the global momentum $\rho\mathbf{v} + \varepsilon_0\mathbf{E} \times \mathbf{B}$ is a conservative property of the physical system composed by the conjoint fluid-dynamics and electromagnetic fields. This profound characteristic of the physical phenomenology is brought to surface by summing together Eqs. (48) and (52) to obtain the balance equation of total momentum

$$\frac{\partial}{\partial t}(\rho\mathbf{v} + \varepsilon_0\mathbf{E} \times \mathbf{B}) = -\nabla \cdot (\rho\mathbf{v}\mathbf{v} - \boldsymbol{\tau} - \boldsymbol{\tau}_M) \quad (53)$$

Equation (53) is equivalent to Eq. (48) and constitutes a valid and, perhaps, more convenient alternative at the moment of performing numerical calculations because it is not burdened by the presence of any production term.

7 Energy-balance equations

7.1 Preliminary considerations

The prerequisite steps in the formulation of balance equations related to the concept of energy, in its entirety and in its variety of kinds, are the identification of the forms that play a role within a specific physical phenomenology and the recognition of the sum of those forms as the total energy. In turn, the subduing of the latter's production \dot{e}_v per unit volume and time to the famous principle of conservation ($\dot{e}_v = 0$) leads to the deduction and, at the same time, the physical interpretation of interesting and important features related to the possible mechanisms of energy conversion.

In the absence of electromagnetic fields, the typical forms of energy that intervene in hypersonic regime are the kinetic energy possessed by the fluid particles as a consequence of their macroscopic motion and the internal energies distributed over the molecular degrees of freedom of the components. Energy ascribed to intermolecular interactions is systematically neglected. Gravitational energy is not admitted in the picture for the same reason of negligibility adduced in Sec. 6 to justify the omission of the gravitational-field contribution to the body force on the right-hand side of Eq. (48). Under the assumed circumstances, the sum of kinetic energy and

internal energies constitutes the total energy and, as such, that sum acquires the prerogative of being conservative. The situation changes drastically in the presence of the electromagnetic field. The kinetic energy and the internal energies associated with matter are still part of the scene but their sum, which will be referred to as *matter energy* for consistency with the terminology introduced in Sec. 6 when dealing with momentum, does not exhaust the totality of forms. The electromagnetic field possesses energy in the same way as it does for momentum. It turns out, therefore, that there is a further kind of energy to account for: the *electromagnetic energy*. It is the sum of matter energy and electromagnetic energy to provide the total energy in this case and to be characterized by a vanishing production. It will be shown in the sequel that, once again, the Maxwell equations [Eqs. (36) and (37)] and their adequately manipulated blend with the balance equations of kinetic energy and internal energies play a fundamental role in the achievement of the outlined understanding of the physical situation.

7.2 Kinetic energy

The kinetic-energy balance equation

$$\frac{\partial}{\partial t} \left(\rho \frac{\mathbf{v}^2}{2} \right) + \nabla \cdot \left(\rho \frac{\mathbf{v}^2}{2} \mathbf{v} \right) = \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) - \boldsymbol{\tau} : \nabla \mathbf{v} + \rho_e \mathbf{v} \cdot \mathbf{E} - \mathbf{J}_Q \cdot \mathbf{v} \times \mathbf{B} \quad (54)$$

descends straightforwardly from that of matter momentum simply by scalar-multiplying both sides of Eq. (48) by the velocity vector and by rearranging the resulting right-hand side to reflect the structure of Eq. (16). Inspection of Eq. (54) indicates at once kinetic-energy diffusive flux and production. The latter comprises the habitual contribution that includes the combined action of medium deformation and tensional state, and a contribution originating from the existence of the electromagnetic field. With regard to this additional contribution, the magnetic part contains only the conduction-current density. This is the obvious consequence of the orthogonality $[\mathbf{v} \cdot (\rho_e \mathbf{v} \times \mathbf{B}) = 0]$ between the velocity vector and the part of the body force in Eq. (49) containing the convection-current density that appears explicitly after expanding the electric-current density according to Eq. (33). Equation (54) is, clearly, not an independent equation; it merely represents the projection of Eq. (48) along the local direction of the instantaneous streamlines of the flow field.

7.3 Internal energy

From a thermodynamic point of view, the ionized gas mixture of interest in the present context has to be considered as a composite system whose subsystems, represented by the molecular degrees of freedom possessed by the components, are in

disequilibrium with respect to mass exchanges (chemical reactions) and energy exchanges (thermal relaxations) [39]. In other words, the internal energies distributed over the molecular degrees of each component must be introduced and accounted for separately. In general, the i -th component owns ℓ_i independent molecular degrees of freedom ($\delta = 1, \dots, \ell_i$) and the δ -th degree of freedom features its private internal energy $U_{i\delta}$. It appears worthwhile, incidentally, to mention that the problem of the explicit separation of the molecular degrees of freedom in independent entities at the level of the internal Schrödinger equation of the molecules is still an open issue in demand of satisfactory resolution and is systematically glossed over by making recourse to the poor, and incorrect, classical separation in electronic, vibrational, rotational (and etc) molecular degrees of freedom. This is certainly a gap that calls for enhancement of basic understanding achievable only through advanced research. The pointed-out limitation, however, does not prevent the development of a formal equation framework. The independence of the degrees of freedom implies the additivity of the internal energies

$$U = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} U_{i\delta} \quad (55)$$

Equation (55) gives the internal energy of the gas mixture and can be conveniently rephrased in terms of specific quantities as

$$\rho u = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \rho_i u_{i\delta} \quad (56)$$

The specificity of $u_{i\delta}$ refers to the unit mass of the i -th component while the specificity of u refers to the unit total mass. On the fluid-dynamics side, the $\sum_{i=1}^n \ell_i$ specific internal energies $u_{i\delta}$ are unknowns of the flow field and their determination can be achieved through the following $\sum_{i=1}^n \ell_i$ balance equations

$$\frac{\partial \rho_i u_{i\delta}}{\partial t} + \nabla \cdot (\rho_i u_{i\delta} \mathbf{v}) = -\nabla \cdot \mathbf{J}_{U_{i\delta}} + \dot{u}_{v,i\delta} \quad (57)$$

$$\delta = 1, \dots, \ell_i; i = 1, \dots, n$$

The diffusive fluxes and productions appearing on the right-hand side of Eq. (57) require the assignment of phenomenological relations. With regard to the productions, it will be shown in Sec. 7.4 that only $\sum_{i=1}^n \ell_i - 1$ of them are independent in consequence of the principle of total-energy conservation. On the thermodynamics side, the specific internal energies $u_{i\delta}$ are linked to the Helmholtz potentials

$f_{i\delta}(T_{i\delta}, v_i)$ that describe the thermodynamic behaviour of the molecular degrees of freedom via their dependence on the corresponding temperatures $T_{i\delta}$ and on the specific volumes v_i of the components. The link takes the form

$$u_{i\delta} = -T_{i\delta}^2 \left(\frac{\partial f_{i\delta}/T_{i\delta}}{\partial T_{i\delta}} \right)_{v_i} = u_{i\delta}(T_{i\delta}, v_i) \quad (58)$$

$$\delta = 1, \dots, \ell_i; i = 1, \dots, n$$

Each of the $\sum_{i=1}^n \ell_i$ thermodynamic relations (58) provides the functional dependence to obtain the temperature $T_{i\delta}$ for prescribed specific internal energy $u_{i\delta}$ and specific volume ($v_i = 1/\rho_i$) of the i -th component. The set of the functions $f_{i\delta}(T_{i\delta}, v_i)$ characterizes the global thermodynamic model [39] of the gas mixture. Their explicit determination presupposes the knowledge of appropriate partition functions [56,57] whose construction, in turn, belongs to the domain of statistical thermodynamics (Refs. [56–59] and references therein). It ought to be remarked that the described equation scheme is founded on the assumption that the population distributions over the quantum-energy states associated with the molecular degrees of freedom can be represented in analytical form, the Boltzmann distribution being a particular case. This assumption is critical for the effectiveness of Eq. (57) and the validity of Eq. (58). Circumstances cannot be excluded in which this assumption becomes untenable. In that case, a deeper characterization of the thermal relaxations, with repercussions on the chemical kinetics of the gas mixture, becomes necessary because the quantum-state populations are themselves unknowns subjected to balance equations that deal with state-to-state exchanges of energy and mass. A substantial body of works (Refs. [60–64] and references therein) addressing the state-to-state phenomenology has been growing recently but the methods elaborated so far are not yet completely free from difficulties of conceptual and computational nature. However, these difficulties notwithstanding, experimental and computational evidence (Refs. [65,66] and references therein) of the existence of non-analytical distributions of the quantum-state populations points towards the conclusion that the avenue of state-to-state thermal kinetics certainly deserves to be explored with vigorous effort for reasons of both scientific and engineering interest. This topic will not be elaborated further here because it is beyond the scope of the present context. Interested readers are referred to the cited literature.

Taking into account the additivity [Eq. (56)] of the internal energies, the balance equation of the gas-mixture internal energy

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{v}) = -\nabla \cdot (\rho u \mathbf{J}_u) + \dot{u}_v \quad (59)$$

is easily deduced from the summation of Eq. (57) on the subscripts i, δ . The internal-energy diffusive flux and production on the right-hand side of Eq. (59) read respectively

$$\mathbf{J}_U = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \mathbf{J}_{U_{i\delta}} \quad (60)$$

$$\dot{u}_v = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \dot{u}_{v,i\delta} \quad (61)$$

Equation (59) is not in its final form. There is more to say about the internal-energy production in consequence of the principle of total-energy conservation. The completion will be done in Sec. 7.4.

Thermal equilibrium prevails when all temperatures $T_{i\delta}$ equalize to a common temperature T . This situation should arise as a particular solution of the multi-temperature scheme embodied in Eqs. (57) and (58), assuming that the component internal-energy diffusive fluxes and productions are correctly prescribed. An alternative approach, possible when there is sufficient (experimental) evidence that supports the idea as a useful approximation accurate enough to reflect realism, consists in the presumptive imposition of thermal equilibrium as a shortcut to spare the numerical costs of dealing with the mathematical complexity of Eqs. (57) and (58). In this manner, the details associated with Eq. (57) are given up and Eq. (59) is used directly for the determination of the gas-mixture specific internal energy with the provision that, now, a phenomenological relation is needed for the internal-energy diffusive flux appearing on the left-hand side of Eq. (60). A phenomenological relation for the internal-energy production appearing on the left-hand side of Eq. (61) is not needed because its expression is fixed by the imposition of total-energy conservation (see Sec. 7.4). Obviously, the thermodynamic relations (58) are still applicable with $T_{i\delta} = T$; thus, the temperature of the gas mixture follows from the resolution of

$$\rho u = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \rho_i u_{i\delta}(T, v_i) \quad (62)$$

7.4 Matter energy

According to the considerations of Sec. 7.1, specific matter energy is defined as the sum

$$e_m = u + \frac{v^2}{2} \quad (63)$$

of kinetic energy and gas-mixture internal energy. The corresponding balance equation

$$\frac{\partial \rho e_m}{\partial t} + \nabla \cdot (\rho e_m \mathbf{v}) = -\nabla \cdot (\mathbf{J}_U - \boldsymbol{\tau} \cdot \mathbf{v}) \\ + \dot{u}_v - \boldsymbol{\tau} : \nabla \mathbf{v} + \rho_c \mathbf{v} \cdot \mathbf{E} - \mathbf{J}_Q \cdot \mathbf{v} \times \mathbf{B} \quad (64)$$

follows, therefore, from the sum of Eqs. (54) and (59). The inspection of the right-hand side of Eq. (64) provides the matter-energy diffusive flux

$$\mathbf{J}_{Em} = \mathbf{J}_U - \boldsymbol{\tau} \cdot \mathbf{v} \quad (65)$$

and production

$$\dot{e}_{m,v} = \dot{u}_v - \boldsymbol{\tau} : \nabla \mathbf{v} + \rho_c \mathbf{v} \cdot \mathbf{E} - \mathbf{J}_Q \cdot \mathbf{v} \times \mathbf{B} \quad (66)$$

In the presence of the electromagnetic field, one is not entitled to assume the matter-energy production as unconditionally vanishing. The further addendum to account for is the production of the electromagnetic energy

$$\dot{e}_{em,v} = -\mathbf{j} \cdot \mathbf{E} \quad (67)$$

Its expression derives from arguments related to the work done by the electromagnetic field when electric charges are displaced within it [40]. So, for consistency with the physical phenomenology, the principle of total-energy conservation must be enforced as

$$\dot{e}_{m,v} + \dot{e}_{em,v} = 0 \quad (68)$$

The substitution of Eqs. (66) and (67), the latter expanded according to Eq. (33), into Eq. (68) leads to the following important, full of physical significance, expression of the internal-energy production

$$\dot{u}_v = \boldsymbol{\tau} : \nabla \mathbf{v} + \mathbf{J}_Q \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (69)$$

The *Joule effect* appears naturally in Eq. (69) and is represented by the electromagnetic term linked exclusively to the conduction-current density. With regard to this point, it seems worth mentioning that sometimes the electromagnetic term on the right-hand side of Eq. (67) is erroneously confused as being responsible for the Joule effect. An important conclusion to be drawn from Eq. (69), with a view to Eq. (61), is that not only the combined action of medium deformation and

tensional state but also the flowing of a conduction current through the electromagnetic field concurs to induce non-equilibrium excitation of the molecular degrees of freedom. How the repartition of the converted amount of energy takes place among the molecular degrees of freedom can be ascertained only when the expressions of the productions $\dot{u}_{v,i\delta}$ are explicitly known. In any case, Eqs. (61) and (69) together indicate that in multi-temperature circumstances, only $\sum_{i=1}^n \ell_i - 1$ productions need the assignment of phenomenological relations, and that such a necessity does not exist in the event of thermal equilibrium.

The availability of Eq. (69) leads to recast Eq. (64) into the final form

$$\frac{\partial \rho e_m}{\partial t} + \nabla \cdot (\rho e_m \mathbf{v}) = -\nabla \cdot (\mathbf{J}_U - \boldsymbol{\tau} \cdot \mathbf{v}) + \mathbf{j} \cdot \mathbf{E} \quad (70)$$

and to the completion of the balance equation [Eq. (59)] of the gas-mixture internal energy which now reads

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{v}) = -\nabla \cdot \mathbf{J}_U + \boldsymbol{\tau} : \nabla \mathbf{v} + \mathbf{J}_Q \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (71)$$

Equation (70) or Eq. (71) can replace anyone of Eq. (57) in the set of the governing equations.

7.5 Electromagnetic energy

The recognition of the existence of the electromagnetic energy and the derivation of its associated balance equation are achieved by following a procedure very similar to the one worked out for the electromagnetic momentum, that is, through a skillful transformation [40,43,46,47] of the electromagnetic-energy production [Eq. (67)] by taking advantage of the Maxwell equations [Eqs. (36) and (37)]. Appendix D provides the mathematical details. The final result already cast in accordance with Eq. (14) reads

$$\frac{\partial}{\partial t} \left[\frac{\epsilon_0}{2} (E^2 + c^2 B^2) \right] = -\nabla \cdot (\epsilon_0 c^2 \mathbf{E} \times \mathbf{B}) - \mathbf{j} \cdot \mathbf{E} \quad (72)$$

Equation (72) indicates explicitly that the electromagnetic field contains energy distributed in space with density $\frac{\epsilon_0}{2} (E^2 + c^2 B^2)$, transported through space with flux given by the Poynting vector $\epsilon_0 c^2 \mathbf{E} \times \mathbf{B}$, and exchanged with the energy of matter with the production rate $-\mathbf{j} \cdot \mathbf{E}$. Once again, Eq. (72) is not an independent equation; there is no new physical information in it that is not already contained in

the Maxwell equations. The considerations made in this regard with respect to the balance equation of electromagnetic momentum [Eq. (52)] apply here unvaried.

Equation (72) reflects the structure of Eq. (14) but there have been attempts [13,14] to adapt it for the purpose of fitting the structure of Eq. (16). The adaptation is based on the transformation of electric-field intensity and magnetic induction between two reference systems in the non-relativistic approximation

$$\mathbf{E}' = \mathbf{E} + \mathbf{v} \times \mathbf{B} \quad (73)$$

$$\mathbf{B}' = \mathbf{B} - \frac{1}{c^2} \mathbf{v} \times \mathbf{E} \quad (74)$$

The primed reference system is identified with the one attached to the generic fluid particle during its motion. The basic step is the evaluation of the Poynting vector in the primed reference system [13,14,20]

$$\varepsilon_0 c^2 \mathbf{E}' \times \mathbf{B}' = \varepsilon_0 c^2 \mathbf{E} \times \mathbf{B} - \frac{\varepsilon_0}{2} (E^2 + c^2 B^2) \mathbf{v} + \boldsymbol{\tau}_M \cdot \mathbf{v} \quad (75)$$

by taking advantage of the transformations (73) and (74). Appendix E contains the mathematical details. It is then a simple matter to solve Eq. (75) for $\varepsilon_0 c^2 \mathbf{E} \times \mathbf{B}$ and to substitute the resulting expression into Eq. (72) to obtain an alternative balance equation of the electromagnetic energy

$$\begin{aligned} \frac{\partial}{\partial t} \left[\frac{\varepsilon_0}{2} (E^2 + c^2 B^2) \right] + \nabla \cdot \left[\frac{\varepsilon_0}{2} (E^2 + c^2 B^2) \mathbf{v} \right] = \\ - \nabla \cdot (\varepsilon_0 c^2 \mathbf{E}' \times \mathbf{B}' - \boldsymbol{\tau}_M \cdot \mathbf{v}) - \mathbf{j} \cdot \mathbf{E} \end{aligned} \quad (76)$$

Equation (76) reflects the structure of Eq. (16) and shows an interesting and remarkable similarity with Eq. (70). From its perspective, electromagnetic energy is *convected* with matter and diffused with flux $\varepsilon_0 c^2 \mathbf{E}' \times \mathbf{B}' - \boldsymbol{\tau}_M \cdot \mathbf{v}$. This viewpoint shares many analogies with the one discussed in Sec. 5 in relation to the magnetic-induction equation [Eq. (40)]. In this case also, there is a conceptual objection, already hinted at by Napolitano [16], that obscures the appeal of this adaptation and of its consequent interpretation. The transformations (73) and (74) are rigorously valid only between two reference systems in uniform rectilinear motion with respect to each other. Thus, they are not complete if the primed reference system is attached to the generic fluid particle because the latter is accelerated ($\mathbf{a} = \partial \mathbf{v} / \partial t + \mathbf{v} \cdot \nabla \mathbf{v}$). As explicitly emphasized by Feynman [40], transformations of electric-field intensity and magnetic induction between two reference systems in relative accelerated motion do depend on the acceleration. One may wonder whether or not the terms connected with acceleration that should appear in Eqs. (73) and (74) are negligible in the non-relativistic approximation. Besides the fact that general transformations including acceleration seem to be found nowhere

in the literature, the question appears to be a moot argument not worth grappling with because even if a positive answer is found, one cannot reconcile Eq. (76) with the physical fact that the electromagnetic field and its properties momentum and energy are attached to space.

7.6 Total energy

According to Eq. (68), all the electromagnetic energy that disappears locally reappears as matter energy or viceversa, exactly in the same guise of what happens to momentum. The sum of Eqs. (70) and (72), therefore, provides the balance equation of total energy

$$\frac{\partial}{\partial t} [\rho e_m + \frac{\varepsilon_0}{2} (E^2 + c^2 B^2)] = -\nabla \cdot (\rho v e_m + \mathbf{J}_u - \boldsymbol{\tau} \cdot \mathbf{v} + \varepsilon_0 c^2 \mathbf{E} \times \mathbf{B}) \quad (77)$$

For the purpose of numerical calculations, Eq. (77) is perfectly equivalent to either Eq. (70) or Eq. (71) but, on the contrary of the latter equations, it does not present any burdensome production term.

7.7 Mechanisms of energy conversion

A summary of the productions relative to kinetic energy, internal energy and electromagnetic energy is illustrated in Table 1. The electromagnetic-energy production [Eq. (67)] has been expanded according to Eq. (33). The tabulation gives a visual representation of the possible mechanisms of energy conversion. Thus, electromagnetic energy is converted partly in kinetic energy ($\rho_c \mathbf{v} \cdot \mathbf{E}$) through the action of the electric field on the convection current and partly in internal energy ($\mathbf{J}_Q \cdot \mathbf{E}$) through the action of the electric field on the conduction current. In turn, kinetic energy is converted in internal energy via the interplay between medium deformation and tensional state ($\boldsymbol{\tau} : \nabla \mathbf{v}$), and through the combined action of the conduction current and the magnetic induction ($\mathbf{J}_Q \cdot \mathbf{v} \times \mathbf{B}$). The Joule effect [$\mathbf{J}_Q \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B})$] is the conjoint manifestation of two different conversion mechanisms of, respectively, electromagnetic and kinetic nature. A more complete characterization of the energy-conversion schematism illustrated in Table 1 covering aspects of reversibility and irreversibility presupposes the explicit knowledge of the entropy production. By definition, the latter identifies the irreversible processes and, being subdued to the second law of thermodynamics that guarantees its non-negativity, imposes an inviolable direction arrow on some of the conversion pathways existing among the corresponding terms in Table 1. The entropy production will be dealt with in Sec. 9.2.

Table 1

Mechanisms of energy conversion.

energy form	production		
kinetic	$-\boldsymbol{\tau} : \nabla \mathbf{v}$	$+\rho_c \mathbf{v} \cdot \mathbf{E}$	$-\mathbf{J}_Q \cdot \mathbf{v} \times \mathbf{B}$
internal	$+\boldsymbol{\tau} : \nabla \mathbf{v}$	$+\mathbf{J}_Q \cdot \mathbf{E}$	$+\mathbf{J}_Q \cdot \mathbf{v} \times \mathbf{B}$
electromagnetic		$-\rho_c \mathbf{v} \cdot \mathbf{E}$	$-\mathbf{J}_Q \cdot \mathbf{E}$

8 Concluding considerations related to the governing equations in open form

The governing equations in open form surveyed in the preceding sections embrace the physical phenomenology comprising the hypersonic flow field of an ionized, but not polarized and magnetized, gas mixture and the presence of the electromagnetic field. For quick reference, they are summarized in Tables 2–5 according to several alternative but physically equivalent options. Regardless of the selected option, the set of equations is not operative yet because it contains the variables requiring the assignment of phenomenological relations. These variables identify the fundamental disciplines that converge into the foundational framework on which hypersonics rests, namely thermodynamics ($f_{i\delta}$), chemical kinetics (ξ_k), thermal kinetics ($\dot{u}_{v,i\delta}$), diffusion theory ($\mathbf{J}_{m_i}, \boldsymbol{\tau}, \mathbf{J}_{U_{i\delta}}$), and call for the selection of models apt to represent in an as accurate as possible manner the physical behaviour manifested by a given real medium under the specific circumstances characteristic of a given application. The latter requirement materializes through the assignment of the thermodynamic model (all $f_{i\delta}$) for the gas mixture and of the phenomenological relations establishing the link between the unknowns $\xi_k, \dot{u}_{v,i\delta}, \mathbf{J}_{m_i}, \boldsymbol{\tau}, \mathbf{J}_{U_{i\delta}}$ and the basic unknowns, and/or their gradients, of the flow field. Only then, the equations in the governing set acquire the prerequisite closed form necessary to proceed towards the achievement of their mathematical solution. It seems appropriate at this point to emphasize that the seemingly *incomplete* character of the governing set in open form should not hinder at all the development of algorithms for the numerical solution of the differential equations that belong to the set. On the contrary, such a development is highly desirable. As a matter of fact, it will never be stressed enough how much convenient it is for the efficient resolution of the flow field that algorithm-development studies would concentrate on the governing set in open form as main target. This is a proposition that certainly implies an ambitious programme but the prospective benefits are too appealing to be ignored and the idea to be hurriedly dismissed. If such a programme succeeds then the phenomenological relations become relegated to the role of *subroutines*, interchangeable according to the specific necessities of a given application, and the architecture of the numerical kernel will feature the extraordinary useful flexibility of being generally applicable and independent from the specific physical behaviour of the real medium.

Table 2
 Governing equations relative to gas-mixture composition

equations	Eq.	unknowns	no. of equations or sub. range
$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}) = -\nabla \cdot \mathbf{J}_{m_i} + \sum_{k=1}^r \dot{\xi}_k \nu_{ki} M_i$	(17)	ρ_i	$i = 1, \dots, n-s$
$\frac{\partial \rho_j^*}{\partial t} + \nabla \cdot (\rho_j^* \mathbf{v}) = -\nabla \cdot \mathbf{J}_{m_j^*}$	(22)	ρ_j^*	$j = 1, \dots, s$
$\mathbf{J}_{m_j^*} = \sum_{i=1}^n \frac{1}{M_i} \mathbf{J}_{m_i} \sigma_{ij} M_j^*$	(23)	$\mathbf{J}_{m_j^*}$	$j = 1, \dots, s$
$\hat{\rho}_j^* = \rho_j^* - \sum_{i=1}^{n-s} \frac{\rho_i}{M_i} \sigma_{ij} M_j^*$	(27)	$\hat{\rho}_j^*$	$j = 1, \dots, s$
$\rho_i = \sum_{j=1}^s \hat{\rho}_j^* \hat{\sigma}_{ji}^{-1}$	(29)	ρ_i	$i = n-s+1, \dots, n$
$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$	(21)	ρ	1
$\rho_c = -e N_A \sum_{i=1}^n \frac{\rho_i}{M_i} \sigma_{is}$	(13)	ρ_c	1
$\mathbf{J}_Q = -e N_A \sum_{i=1}^n \frac{1}{M_i} \mathbf{J}_{m_i} \sigma_{is}$	(31)	\mathbf{J}_Q	3
$\mathbf{j} = \rho_c \mathbf{v} + \mathbf{J}_Q$	(33)	\mathbf{j}	3

The construction of the thermodynamic model is a task belonging to the realm of statistical thermodynamics (see Sec. 7.3). There are a few options available concerning the derivation of the phenomenological relations for the unknown productions and diffusive fluxes. One can seek recourse to irreversible thermodynamics [20–24,35–37,67–70], to the more sophisticated kinetic theory of gases [71–77] or to experimental investigation. In practice, the phenomenological relations emerge as the outcome of a concerted effort involving all three options to different degrees of depth. The approach relying on irreversible thermodynamics is preferable *to get started* in the derivation endeavour because, although its findings may have sometimes narrow limits of validity from a *quantitative* point of view, it proceeds in a conceptually straightforward manner from the exploitation of the entropy production and of the second law of thermodynamics, it is not affected (not to the same extent, at least) by the overwhelming mathematical cumbersomeness and complex-

Table 3
 Governing equations relative to momentum

equations	Eq.	unknowns	no. of equations
$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \boldsymbol{\tau} + \rho_c \mathbf{E} + \mathbf{j} \times \mathbf{B}$	(48)	\mathbf{v}	3
or			
$\frac{\partial}{\partial t}(\rho \mathbf{v} + \varepsilon_0 \mathbf{E} \times \mathbf{B}) = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} - \boldsymbol{\tau} - \boldsymbol{\tau}_M)$	(53)	\mathbf{v}	3
$\boldsymbol{\tau}_M = \varepsilon_0(\mathbf{E}\mathbf{E} - \frac{1}{2}E^2\mathbf{U}) + \varepsilon_0 c^2(\mathbf{B}\mathbf{B} - \frac{1}{2}B^2\mathbf{U})$	(51)	$\boldsymbol{\tau}_M$	6

ity of the detailed kinetic theories and, above all, it offers a depth of insight that goes a long way in the direction of understanding the transport processes at work in the flow field and of recognizing the associated driving forces.

9 Linear irreversible thermodynamics

9.1 Preliminary remarks

The linear theory of irreversible thermodynamics will be revisited in the following sections in conformity with the prescription of thermal equilibrium. The assumption that thermal equilibrium prevails among the molecular degrees of freedom of the components is a recurrent characteristic shared by authors that follow the irreversible-thermodynamics approach. Some [23,37] even go further and assume mechanical equilibrium. Thermal equilibrium implies the possibility of dealing with one single temperature and, obviously, brings in great simplification; on the other hand, it restricts the applicability domain of the ensuing phenomenological relations. The sole attempts the present author is aware of that ventured into a thermal-disequilibrium analysis were made by Woods [22], Napolitano [35,36], and Morro and Romeo [78–80]. However, the treatments proposed by Woods and by Napolitano share similarities that contain elements, bearing on the definition of the driving forces connected with the occurrence of multiple temperatures, apparently not yet completely freed from conceptual objections. Similarly, Morro and Romeo did not consider the internal structure of the molecules; in other words, they implicitly assumed for each component the thermal equilibrium among its molecular degrees of freedom. More work is certainly needed to improve knowledge in this department of irreversible thermodynamics. The motivation justifying the choice adopted here resides mainly in the intention to put the emphasis on

Table 4

Governing equations relative to energy

equations	Eq.	unknowns	no. of equations or sub. range
$\frac{\partial \rho_i u_{i\delta}}{\partial t} + \nabla \cdot (\rho_i u_{i\delta} \mathbf{v}) = -\nabla \cdot \mathbf{J}_{U_{i\delta}} + \dot{u}_{v,i\delta}$	(57)	$u_{i\delta}$	$\delta = 1, \dots, \ell_i$ $i = 1, \dots, n$
$u_{i\delta} = -T_{i\delta}^2 \left(\frac{\partial f_{i\delta}/T_{i\delta}}{\partial T_{i\delta}} \right)_{v_i} = u_{i\delta}(T_{i\delta}, v_i)$	(58)	$T_{i\delta}$	$\delta = 1, \dots, \ell_i$ $i = 1, \dots, n$
$v_i = 1/\rho_i$		v_i	$i = 1, \dots, n$
$\rho u = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \rho_i u_{i\delta}$	(56)	u	1
$e_m = u + \frac{v^2}{2}$	(63)	e_m	1
or			
$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{v}) =$ $- \nabla \cdot \mathbf{J}_U + \boldsymbol{\mathcal{T}} : \nabla \mathbf{v} + \mathbf{J}_Q \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B})$	(71)	u	1
$\mathbf{J}_U = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \mathbf{J}_{U_{i\delta}}$	(60)	\mathbf{J}_U	3
$\frac{\partial \rho_i u_{i\delta}}{\partial t} + \nabla \cdot (\rho_i u_{i\delta} \mathbf{v}) = -\nabla \cdot \mathbf{J}_{U_{i\delta}} + \dot{u}_{v,i\delta}$	(57)	$u_{i\delta}$	$\sum_{i=1}^n \ell_i - 1$
$\rho u = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \rho_i u_{i\delta}$	(56)	$u_{i\delta}$	1
$u_{i\delta} = -T_{i\delta}^2 \left(\frac{\partial f_{i\delta}/T_{i\delta}}{\partial T_{i\delta}} \right)_{v_i} = u_{i\delta}(T_{i\delta}, v_i)$	(58)	$T_{i\delta}$	$\delta = 1, \dots, \ell_i$ $i = 1, \dots, n$
$v_i = 1/\rho_i$		v_i	$i = 1, \dots, n$
$e_m = u + \frac{v^2}{2}$	(63)	e_m	1

the peculiarities of the physical phenomenology connected with the existence of the electromagnetic field and, for that purpose, to keep the mathematical analysis relieved from tangential or, even, unnecessary complexity. Nevertheless, the multi-temperature phenomenology is quantitatively important in hypersonic applications and should not be forgotten.

Table 4
Continued

equations	Eq.	unknowns	no. of equations or sub. range
or			
$\frac{\partial \rho e_m}{\partial t} + \nabla \cdot (\rho e_m \mathbf{v}) = -\nabla \cdot (\mathbf{J}_U - \boldsymbol{\tau} \cdot \mathbf{v}) + \mathbf{j} \cdot \mathbf{E}$	(70)	e_m	1
$\mathbf{J}_U = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \mathbf{J}_{U_{i\delta}}$	(60)	\mathbf{J}_U	3
$\frac{\partial \rho_i u_{i\delta}}{\partial t} + \nabla \cdot (\rho_i u_{i\delta} \mathbf{v}) = -\nabla \cdot \mathbf{J}_{U_{i\delta}} + \dot{u}_{v,i\delta}$	(57)	$u_{i\delta}$	$\sum_{i=1}^n \ell_i - 1$
$\rho u = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \rho_i u_{i\delta}$	(56)	$u_{i\delta}$	1
$u_{i\delta} = -T_{i\delta}^2 \left(\frac{\partial f_{i\delta}/T_{i\delta}}{\partial T_{i\delta}} \right)_{v_i} = u_{i\delta}(T_{i\delta}, v_i)$	(58)	$T_{i\delta}$	$\begin{matrix} \delta = 1, \dots, \ell_i \\ i = 1, \dots, n \end{matrix}$
$v_i = 1/\rho_i$		v_i	$i = 1, \dots, n$
$e_m = u + \frac{v^2}{2}$	(63)	u	1
or			
$\frac{\partial}{\partial t} [\rho e_m + \frac{\varepsilon_0}{2} (E^2 + c^2 B^2)] = -\nabla \cdot (\rho \mathbf{v} e_m + \mathbf{J}_U - \boldsymbol{\tau} \cdot \mathbf{v} + \varepsilon_0 c^2 \mathbf{E} \times \mathbf{B})$	(77)	e_m	1
$\mathbf{J}_U = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \mathbf{J}_{U_{i\delta}}$	(60)	\mathbf{J}_U	3
$\frac{\partial \rho_i u_{i\delta}}{\partial t} + \nabla \cdot (\rho_i u_{i\delta} \mathbf{v}) = -\nabla \cdot \mathbf{J}_{U_{i\delta}} + \dot{u}_{v,i\delta}$	(57)	$u_{i\delta}$	$\sum_{i=1}^n \ell_i - 1$
$\rho u = \sum_{i=1}^n \sum_{\delta=1}^{\ell_i} \rho_i u_{i\delta}$	(56)	$u_{i\delta}$	1
$u_{i\delta} = -T_{i\delta}^2 \left(\frac{\partial f_{i\delta}/T_{i\delta}}{\partial T_{i\delta}} \right)_{v_i} = u_{i\delta}(T_{i\delta}, v_i)$	(58)	$T_{i\delta}$	$\begin{matrix} \delta = 1, \dots, \ell_i \\ i = 1, \dots, n \end{matrix}$
$v_i = 1/\rho_i$		v_i	$i = 1, \dots, n$
$e_m = u + \frac{v^2}{2}$	(63)	u	1

Table 5

Governing equations relative to the electromagnetic field

equations	Eq.	unknowns	no. of equations
$\frac{\partial \mathbf{B}}{\partial t} + \nabla \times \mathbf{E} = 0$	(36)	\mathbf{B}	3
$\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} - \varepsilon_0 c^2 \nabla \times \mathbf{B} = -\mathbf{j}$	(37)	\mathbf{E}	3
or			
$\frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = \nabla^2 \phi + \frac{\rho_c}{\varepsilon_0}$	(44)	ϕ	1
$\frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = \nabla^2 \mathbf{A} + \frac{1}{\varepsilon_0 c^2} \mathbf{j}$	(45)	\mathbf{A}	3
$\mathbf{B} = \nabla \times \mathbf{A}$	(43)	\mathbf{B}	3
$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}$	(42)	\mathbf{E}	3

9.2 Entropy-balance equation and entropy production

The thermodynamics of the irreversible processes hinges on the entropy balance equation

$$\frac{\partial \rho \mathcal{J}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathcal{J}) = -\nabla \cdot \mathbf{J}_s + \dot{\mathcal{J}}_v \quad (78)$$

Equation (78) represents a formal balance involving entropy density \mathcal{J} , diffusive flux \mathbf{J}_s , and production $\dot{\mathcal{J}}_v$, and acquires operational character only after that entropy diffusive flux and production are given more explicit expressions. This is achieved by taking advantage of the thermodynamic fundamental relation [24,39,68,81] of the gas mixture in the entropic formulation which, under the assumption of thermal equilibrium, reads formally

$$\mathcal{J} = \mathcal{J}(u, v, \alpha_1, \alpha_2, \dots, \alpha_n) \quad (79)$$

In Eq. (79), $v = 1/\rho$ is the specific volum of the gas mixture. In view of the forthcoming analysis, it is appropriate to recall that the first derivatives of the function (79) represent the state equations in the entropic scheme and define, respectively, temperature, pressure and chemical potentials

$$\frac{1}{T} = \left(\frac{\partial \mathcal{J}}{\partial u} \right)_{v,\alpha} \quad (80)$$

$$\frac{p}{T} = \left(\frac{\partial \mathcal{J}}{\partial v} \right)_{s,\alpha} \quad (81)$$

$$-\frac{\mu_i}{T} = \left(\frac{\partial \mathcal{J}}{\partial \alpha_i} \right)_{u,v,\alpha_j \neq i} \quad i = 1, \dots, n \quad (82)$$

of the gas mixture. Also, for reasons of simplicity in the notation, it is convenient to work out the mathematical details with the aid of the substantial-derivative operator $D/Dt = \partial/\partial t + \mathbf{v} \cdot \nabla$, whose intervention in the balance equations stems from the equivalence [recall also Eq. (16)]

$$\frac{\partial \rho g}{\partial t} + \nabla \cdot (\rho \mathbf{v} g) = \rho \frac{Dg}{Dt} \quad (83)$$

Equation (83) is a direct consequence of total-mass conservation [Eq. (21)]. Taking into account the definitions (80)–(82), the application of the substantial-derivative operator to the function (79) leads to

$$\rho \frac{D\mathcal{J}}{Dt} = \frac{1}{T} \rho \frac{Du}{Dt} + \frac{p}{T} \rho \frac{Dv}{Dt} - \sum_{i=1}^n \frac{\mu_i}{T} \rho \frac{D\alpha_i}{Dt} \quad (84)$$

The steps to achieve the explicit form of the entropy-balance equation appear now evident. The first step consists in obtaining the volume-balance equation. The quickest way is to set $g \equiv v$ in Eq. (83) and to take into account that $\rho v = 1$; hence

$$\rho \frac{Dv}{Dt} = \nabla \cdot \mathbf{v} \quad (85)$$

Counterintuitively as it may appear at first sight, the term on the right-hand side of Eq. (85) does not represent the divergence of the diffusive flux of volume because, by its very definition, a diffusive flux cannot depend on the velocity vector [see Eq. (15)]; this inescapable requirement suggests that a volume-production ($\dot{v}_v = \nabla \cdot \mathbf{v}$) interpretation is the sole possible for the term in question. An alternative explanation reaching the same conclusion can be found in Ref. [19]. The second step involves the substitution of the component-mass balance equations [Eq. (17)], the internal-energy balance equation [Eq. (71)] and the volume-balance equation [Eq. (85)] into Eq. (84), and the consequent rearrangement to reflect the structure of Eq. (78). This brings to the identification of the entropy diffusive flux

$$\mathbf{J}_s = \frac{1}{T} \mathbf{J}_u - \sum_{i=1}^n \frac{\mu_i}{T} \mathbf{J}_{m_i} \quad (86)$$

and of the entropy production

$$\begin{aligned}\dot{\mathcal{A}}_v = & \frac{1}{T} \boldsymbol{\tau} : \nabla \mathbf{v} \\ & - \frac{1}{T^2} (\mathbf{J}_U - \sum_{i=1}^n \mu_i \mathbf{J}_{m_i}) \cdot \nabla T - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_{m_i} \cdot \nabla \mu_i + \frac{1}{T} \mathbf{J}_Q \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \\ & + \frac{p}{T} \nabla \cdot \mathbf{v} - \frac{1}{T} \sum_{k=1}^r \dot{\xi}_k \mathcal{A}_k\end{aligned}\quad (87)$$

The affinities of the chemical reactions are defined as linear combinations

$$\mathcal{A}_k = \sum_{i=1}^n \nu_{ki} M_i \mu_i \quad (88)$$

of the chemical potentials. The entropy production [Eq. (87)] is not in its final form but must be furtherly refined for the purpose of the present context. The refinement consists in performing the standard expansion of the stress and velocity-gradient tensors to bring forth their isotropic, traceless-symmetric (or deviatoric) and anti-symmetric parts. This operation presupposes some familiarity with tensor analysis; extensive help, in this regard, is provided in Refs. [22,23,37,71,74]. The stress tensor separates in the sum

$$\boldsymbol{\tau} = \pi \mathbf{U} + \boldsymbol{\tau}_o^s \quad (89)$$

of the isotropic part, which contains the (scalar) mean normal stress built as the arithmetic average ($\pi = 1/3 \boldsymbol{\tau} : \mathbf{U}$) of the diagonal terms of the stress tensor, and of the traceless-symmetric part $\boldsymbol{\tau}_o^s$. The antisymmetric part of $\boldsymbol{\tau}$ vanishes identically because the stress tensor remains symmetric in the absence of polarization and magnetization. The same expansion performed on the velocity gradient yields

$$\nabla \mathbf{v} = \frac{1}{3} (\nabla \cdot \mathbf{v}) \mathbf{U} + (\nabla \mathbf{v})_o^s + (\nabla \mathbf{v})^a \quad (90)$$

The isotropic part [$1/3(\nabla \cdot \mathbf{v})\mathbf{U}$] describes volume deformation of fluid particles, the traceless symmetric part [$(\nabla \mathbf{v})_o^s$] describes their shape deformation, and the antisymmetric part [$(\nabla \mathbf{v})^a$] describes their rigid rotation with $1/2 \nabla \times \mathbf{v}$ as angular velocity. With the help of relatively simple tensor algebra, it can be shown that, taking into account Eqs. (89) and (90), the first term on the right-hand side of Eq. (87) becomes

$$\boldsymbol{\tau} : \nabla \mathbf{v} = \pi (\nabla \cdot \mathbf{v}) + \boldsymbol{\tau}_o^s : (\nabla \mathbf{v})_o^s \quad (91)$$

The substitution of Eq. (91) and of the expression of the conduction-current density in terms of the component-mass diffusive fluxes [Eq. (31)] into Eq. (87) leads to the desired final form of the entropy production

$$\begin{aligned}
 \dot{\mathcal{J}}_v = & \frac{1}{T} \boldsymbol{\tau}_o^s : (\nabla \mathbf{v})_o^s \\
 & - \frac{1}{T^2} (\mathbf{J}_U - \sum_{i=1}^n \mu_i \mathbf{J}_{m_i}) \cdot \nabla T - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_{m_i} \cdot [\nabla \mu_i + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B})] \\
 & - \frac{1}{T} [-(\pi + p)] \nabla \cdot \mathbf{v} - \frac{1}{T} \sum_{k=1}^r \dot{\xi}_k \mathcal{A}_k
 \end{aligned} \tag{92}$$

In irreversible-thermodynamics parlance, Eq. (92) shows the *generalized fluxes* and the *generalized forces* that produce entropy and, in so doing, identifies the processes responsible for promoting irreversibility in the flow field. In addition to the habitual effects, namely shape $[(\nabla \mathbf{v})_o^s]$ and volume $(\nabla \cdot \mathbf{v})$ deformation of the medium, nonequilibrium chemical reactions ($\mathcal{A}_k \neq 0$), thermal (∇T) and chemical-potential ($\nabla \mu_i$) disuniformities, also the electromagnetic field enlists in the category of the irreversible processes through contributions that add to the chemical-potential gradients and connect to the mass diffusive fluxes of the electrically charged components. Generalized fluxes and forces are summarized in Table 6.

Table 6

Generalized fluxes and forces contributing to the entropy production [Eq. (92)]

flux	force	tensorial order	subscript range
$\boldsymbol{\tau}_o^s$	$(\nabla \mathbf{v})_o^s$	2	
$\frac{1}{T} (\mathbf{J}_U - \sum_{i=1}^n \mu_i \mathbf{J}_{m_i})$	∇T	1	
\mathbf{J}_{m_i}	$\nabla \mu_i + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B})$	1	$i = 1, \dots, n$
$-(\pi + p)$	$\nabla \cdot \mathbf{v}$	0	
$\dot{\xi}_k$	\mathcal{A}_k	0	$k = 1, \dots, r$

The core of irreversible thermodynamics is the exploitation of the expression of the entropy production [Eq. (92)] and of the second law of thermodynamics

$$\dot{\mathcal{J}}_v \geq 0 \tag{93}$$

which endorses its unconditional non-negativity as an ineluctable fact of nature, for the purpose of obtaining suitable expressions of the generalized fluxes in terms of the generalized forces. In this regard, the validity of the Curie postulate is assumed here. The postulate affirms that generalized fluxes of a given tensorial order can depend only on generalized forces of the same tensorial order. This is a simplification because the postulate is rigorously applicable only for isotropic media; that is

not the case in the presence of the electromagnetic field because the existence of the magnetic induction removes the medium isotropy. Thus, the assumption of the postulate validity implies the negligibility of the couplings among each generalized flux and all the generalized forces of different tensorial order. The motivation behind this choice is the same adduced at the end of Sec. 9.1 to justify the assumption of thermal equilibrium, namely the intention to emphasize the essential characteristics due to the presence of the electromagnetic field and, at the same time, minimize mathematical complexity. Readers interested in the general case that includes the neglected cross effects are referred to the specialized literature mentioned in Sec. 8 (Refs. [22,23] in particular). To compensate to some extent for the limitations ensuing from the Curie postulate, the anisotropy imposed on the medium by the magnetic induction will be taken into account in the tensorial nature of the transport coefficients [22,23,71,74,75,77,82–90].

In compliance with the invoked Curie postulate, it is convenient to emphasize the subdivision of the entropy-production terms with same tensorial order by rephrasing Eq. (92) as

$$\dot{\mathcal{J}}_v = \dot{\mathcal{J}}_{v,2} + \dot{\mathcal{J}}_{v,1} + \dot{\mathcal{J}}_{v,0} \quad (94)$$

in which

$$\dot{\mathcal{J}}_{v,2} = \frac{1}{T} \boldsymbol{\tau}_o^s : (\nabla \mathbf{v})_o^s \quad (95)$$

$$\begin{aligned} \dot{\mathcal{J}}_{v,1} = & -\frac{1}{T^2} (\mathbf{J}_U - \sum_{i=1}^n \mu_i \mathbf{J}_{m_i}) \cdot \nabla T \\ & - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_{m_i} \cdot [\nabla \mu_i + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B})] \end{aligned} \quad (96)$$

$$\dot{\mathcal{J}}_{v,0} = -\frac{1}{T} [-(\pi + p)] \nabla \cdot \mathbf{v} - \frac{1}{T} \sum_{k=1}^r \dot{\xi}_k \mathcal{A}_k \quad (97)$$

Given the independence of the three groups (95), (96) and (97), the non-negativity property of the entropy production [Eq. (93)] is passed on to each of them. They will be dealt with separately in the following sections.

9.3 Tensorial (second-order) generalized force

The traceless symmetric part of the velocity gradient is the sole generalized force of second tensorial order that, conjointly with the traceless symmetric part of the

stress tensor, participates in the entropy production [Eq. (95)]

$$\dot{\mathcal{J}}_{v,2} = \frac{1}{T} \boldsymbol{\tau}_o^s : (\nabla \mathbf{v})_o^s \geq 0 \quad (98)$$

The application of the Curie postulate leads to the relatively simple phenomenological relation [22,23,74]

$$\boldsymbol{\tau}_o^s = 2\mu : (\nabla \mathbf{v})_o^s \quad (99)$$

that resembles the more familiar Newton law. The dynamic viscosity μ in Eq. (99) is a fourth-order tensor due to the anisotropy introduced by the magnetic induction. Its determination is beyond the reach of irreversible thermodynamics and it must be considered an import either from the kinetic theory of gases or from experiments. A thorough analysis of the dynamic-viscosity tensor is beyond the purpose of the present context. Here, it is sufficient to recall that most of the 81 scalar coefficients required to compose the tensor turn out to vanish and that its complete characterization is limited to the knowledge of only five scalar coefficients. The sign of some of them must be necessarily positive for compliance with the non-negativity of $\dot{\mathcal{J}}_{v,2}$. References [22,23,74] provided detailed descriptions of structure and properties of the dynamic-viscosity tensor.

9.4 Vectorial generalized forces

Phenomenological relations for vectorial generalized forces arise from the entropy production related to the first tensorial order

$$\begin{aligned} \dot{\mathcal{J}}_{v,1} = & -\frac{1}{T^2} (\mathbf{J}_U - \sum_{i=1}^n \mu_i \mathbf{J}_{m_i}) \cdot \nabla T \\ & - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_{m_i} \cdot [\nabla \mu_i + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B})] \geq 0 \end{aligned} \quad (100)$$

In this regard, one has to confront a multifaceted situation because the combination of generalized fluxes and forces appearing in Eq. (100) is not unique. Different, although equivalent, forms of $\dot{\mathcal{J}}_{v,1}$ exist in consequence of transformations to which fluxes and forces can be subjected, a peculiarity due to the occurrence of mass diffusion and recognized long time ago. The equivalence of the several forms stems from the expectable, and provable, invariance of the phenomenological relations for internal-energy diffusive flux and component-mass diffusive fluxes with respect to the mentioned transformations. On the other hand, the multiplicity of forms implies the non-uniqueness of the heat-flux definition. This fact should not come as

a surprise or be perceived as the manifestation of some inconsistency in the theory because, as appropriately remarked by Napolitano [35,36] in 1969, the

... arbitrariness in the definition of heat flux stems from the fact that any time there is a flux of matter ... there is also a flux of energy ... and it is only a matter of convention (or of convenience) to single out one or more of these fluxes of energy and call them heat flux. ... Any possible definition obviously leaves all physical results unchanged and one should only pay attention in using it consistently, i.e. in associating to it the pertinent expression for the entropy production

...

For a given selection of generalized forces, the heat flux is identified with the generalized flux associated with the temperature gradient. Thus

$$\mathbf{J}'_q = \mathbf{J}_U - \sum_{i=1}^n \mu_i \mathbf{J}_{m_i} = T \mathbf{J}_s \quad (101)$$

is the heat-flux definition compatible with the generalized forces that appear in Eq. (100). Equation (101) is somewhat reminiscent of the classical-thermodynamics relation $dQ = TdS$ but it has received scant attention and its implications on the derivation of the phenomenological relations have rarely been pursued in detail [23,24,68]. Another form of $\dot{\mathcal{J}}_{v,1}$ encountered in the literature [21,23,35–37] is obtained by contracting the terms with the component-mass diffusive fluxes

$$\frac{\mu_i}{T^2} \mathbf{J}_{m_i} \cdot \nabla T - \frac{1}{T} \mathbf{J}_{m_i} \cdot \nabla \mu_i = -\mathbf{J}_{m_i} \cdot \nabla \frac{\mu_i}{T} \quad (102)$$

in Eq. (100). In this way, the latter becomes

$$\dot{\mathcal{J}}_{v,1} = -\frac{1}{T^2} \mathbf{J}_U \cdot \nabla T - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_{m_i} \cdot \left[T \nabla \frac{\mu_i}{T} + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \right] \quad (103)$$

and yields the heat-flux definition

$$\mathbf{J}''_q = \mathbf{J}_U = T \mathbf{J}_s + \sum_{i=1}^n \mu_i \mathbf{J}_{m_i} \quad (104)$$

The overwhelmingly preferred form [23,35–37] of $\dot{\mathcal{J}}_{v,1}$, however, is the one arrived at from the assumption according to which the components of the gas mixture behave as perfect gases. Indeed, in this case the chemical potential can be expressed in terms of specific enthalpy h_i and entropy \mathcal{J}_i of the i -th component

$$\mu_i = h_i - T \mathcal{J}_i \quad (105)$$

and its gradient depends on those of temperature and partial pressure p_i

$$\nabla \mu_i = -\mathcal{J}_i \nabla T + v_i \nabla p_i \quad (106)$$

The substitution of Eqs. (105) and (106) into Eq. (100) leads to the form

$$\begin{aligned} \dot{\mathcal{J}}_{v,1} = & -\frac{1}{T^2} (\mathbf{J}_U - \sum_{i=1}^n h_i \mathbf{J}_{m_i}) \cdot \nabla T \\ & - \frac{1}{T} \sum_{i=1}^n \mathbf{J}_{m_i} \cdot [v_i \nabla p_i + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B})] \end{aligned} \quad (107)$$

with the corresponding heat-flux definition

$$\mathbf{J}_q''' = \mathbf{J}_U - \sum_{i=1}^n h_i \mathbf{J}_{m_i} = T \mathbf{J}_S - T \sum_{i=1}^n \mathcal{J}_i \mathbf{J}_{m_i} \quad (108)$$

The instances considered so far by no means exhaust the list of possibilities. Other choices [37] of the generalized fluxes and forces, together with the identification of the correspondig heat flux, are possible. On the other hand, it is neither necessary nor intended in the present context to embark in an exhaustive survey. The three described forms of $\dot{\mathcal{J}}_{v,1}$ suffice to portray the manifoldness of the heat-flux concept. The irrelevance of its arbitrariness, pointed out in Napolitano's remark, becomes mathematically evident and comprehensible by overturning Eq. (101), Eq. (104) and Eq. (108) as

$$\mathbf{J}_U = \mathbf{J}'_q + \sum_{i=1}^n \mu_i \mathbf{J}_{m_i} = \mathbf{J}''_q = \mathbf{J}'''_q + \sum_{i=1}^n h_i \mathbf{J}_{m_i} \quad (109)$$

and by keeping in mind that the internal-energy diffusive flux is invariant with respect to any possible selection of generalized fluxes, forces and corresponding heat-flux definition. Indeed, it is the internal-energy diffusive flux to be the physical flux that really matters in order to evaluate the thermal energy transferred from the flow field into a body or viceversa.

The derivation of the phenomenological relations of first tensorial order pursued here differs from the habitual treatments found in the literature. It proceeds along a pathway that, starting from a slight adaptation of Eq. (107), establishes a strong parallelism with the Chapman-Enskog method [71–77,82,84–88] of the gas-kinetics theory and enormously facilitates the import of the transport coefficients provided by that method. The transformation that takes care of bringing $\dot{\mathcal{J}}_{v,1}$ into the appropriate form presupposes the temporary replacement of the component-mass diffusive

flux in the term

$$\mathbf{J}_{\text{m}_i} \cdot [v_i \nabla p_i + e N_{\text{A}} \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B})] \quad (110)$$

with the intermediate appearance of the diffusion velocity defined in Eq. (18). After substituting the latter into Eq. (110), taking into account that $\rho_i v_i = 1$, and setting for brevity

$$\mathcal{X}_i = \nabla p_i + e N_{\text{A}} \rho_i \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (111)$$

Eq. (107) can be rephrased as

$$T \dot{\mathcal{J}}_{v,1} = -(\mathbf{J}_{\text{U}} - \sum_{i=1}^n h_i \mathbf{J}_{\text{m}_i}) \cdot \nabla \ln T - \sum_{i=1}^n \mathbf{w}_i \cdot \mathcal{X}_i \quad (112)$$

The advantage of using Eq. (112) rather than Eq. (107) is that the former leads to operate with the central ingredients [71,72,74] of the Chapman-Enskog method, namely the vectors \mathbf{w}_i , \mathcal{X}_i and $\nabla \ln T$. The application of the Curie postulate to Eq. (112) provides the phenomenological relations

$$\mathbf{w}_i = - \sum_{j=1}^n \mathbf{L}_{ij} \cdot \mathcal{X}_j - \mathbf{L}_{iT} \cdot \nabla \ln T \quad (113)$$

$$\mathbf{J}_{\text{U}} - \sum_{i=1}^n h_i \mathbf{J}_{\text{m}_i} = - \sum_{i=1}^n \mathbf{L}_{Ti} \cdot \mathcal{X}_i - \mathbf{L}_{TT} \cdot \nabla \ln T \quad (114)$$

in which the phenomenological coefficients \mathbf{L}_{ij} , \mathbf{L}_{iT} , \mathbf{L}_{Ti} and \mathbf{L}_{TT} are second-order tensors due to the presence of the magnetic induction. Equations (113) and (114) mirror exactly the expressions intervening in the Chapman-Enskog method and, in consequence of that, the tensors \mathbf{L}_{ij} , \mathbf{L}_{iT} , \mathbf{L}_{Ti} and \mathbf{L}_{TT} can be directly and explicitly related as

$$\mathbf{L}_{ij} = -\frac{1}{p} \frac{\rho}{\rho_i} \frac{M_i M_j}{M^2} \mathbf{D}_{ij} \quad (115)$$

$$\mathbf{L}_{iT} = \frac{1}{\rho_i} \mathbf{D}_i^T \quad (116)$$

$$\mathbf{L}_{Ti} = \frac{1}{\rho_i} \tilde{\mathbf{D}}_i^T (-\mathbf{B}) \quad (117)$$

$$\mathbf{L}_{TT} = T \lambda' \quad (118)$$

to the tensors of diffusion \mathbf{D}_{ij} , of thermal diffusion \mathbf{D}_i^T and to the *primed* thermal-conductivity tensor λ' . The prime attached to the thermal-conductivity tensor in Eq. (118) is important: it represents the definition of thermal conductivity consistent with the scalar one that *does not* include the thermodiffusion ratios [72,74]. The latter tensors are styled according to the (scalar) notation of Hirschfelder, Curtiss and Bird [72] only for reasons of convenience related to flow calculations. Yet, the diffusion tensors \mathbf{D}_{ij} in Eq. (115) must be consistent with the convention adopted by Chapman and Cowling {Eqs. (18.2,9) and (18.3,4) in Ref. [71]} and Ferziger and Kaper {Eq. (6.3-24) in Ref. [74]} to fix the indeterminacy of the diffusion-related coefficients appearing in the first-order perturbation of the distribution function in order to make Eq. (113) operational. The diffusion tensors consistent with the indeterminacy-fixing convention adopted by Hirschfelder, Curtiss and Bird {Eq. (7.3-31) in Ref. [72]} are incompatible with Eq. (113) because of the presence in it of the vectors \mathcal{X}_j rather than the vectors {Eq. (18.2,6) in Ref. [71]}

$$\mathbf{d}_j = \nabla x_j + \left(x_j - \frac{\rho_j}{\rho} \right) \nabla \ln p - \frac{\rho_j}{\rho p} (\rho \mathbf{F}_j - \sum_{k=1}^n \rho_k \mathbf{F}_k) \quad (119)$$

habitually employed in kinetic theory and based mainly on the gradients of the molar fractions x_j . In the present case, the external forces in Eq. (119) arise from the electromagnetic field

$$\mathbf{F}_i = -e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (120)$$

Another important reason that justifies this choice was expressed by Ferziger and Kaper [74]

We remark that there is a considerable variation among authors in the nomenclature and definition of the multicomponent diffusion and thermal diffusion coefficients. The definition [adopted by Ferziger and Kaper, as well as Chapman and Cowling] of the multicomponent diffusion coefficients is consistent with Onsager's reciprocity relations of irreversible thermodynamics ... This consistency is of particular importance if one desires to generalize the kinetic theory of gas mixtures to systems in which the number density of each species is not a conserved quantity — e.g., in gas mixtures in which chemical reactions occur between constituents or in polyatomic gases in which transition occur between states with different internal degrees of freedom ... It has been shown ... that, in these cases, it is of importance to choose the definition of the transport coefficients in such a way that they are consistent with Onsager's reciprocity relations and that the definition of the multicomponent diffusion coefficients given [here] is therefore to be preferred to, e.g., the definition given by Hirschfelder, Curtiss and Bird ... Recently, J. Curtiss ... has supported this point of view.

In Eq. (115), M is the average molar mass

$$M = \left(\sum_{i=1}^n \frac{\alpha_i}{M_i} \right)^{-1} = \sum_{i=1}^n M_i x_i \quad (121)$$

of the gas mixture. Equation (117) is an Onsager reciprocal relation. The tilde indicates matrix transposition and the attached functional dependence reminds the necessary inversion of the sign of the magnetic induction. Similar reciprocal relations apply also to the diffusion and thermal-conductivity tensors. However, although important, reciprocity details are not of specific relevance in the present context; interested readers are referred to the specialized literature, particularly the textbooks by Woods [22] and De Groot and Mazur [23].

The phenomenological relations

$$\mathbf{J}_{m_i} = \frac{\rho}{p} \frac{M_i}{M} \sum_{j=1}^n \frac{M_j}{M} \mathbf{D}_{ij} \cdot \mathbf{x}_j - \frac{1}{T} \mathbf{D}_i^T \cdot \nabla T \quad (122)$$

for the component-mass diffusive fluxes follow from the substitution of Eqs. (115) and (116) into Eq. (113) and of the resulting diffusion velocities into Eq. (18). The kinetic-theory result

$$\sum_{i=1}^n M_i \mathbf{D}_{ij} = 0 \quad (123)$$

$$\sum_{i=1}^n \mathbf{D}_i^T = 0 \quad (124)$$

makes the condition (19) identically satisfied. In the same guise, the substitution of Eqs. (117) and (118) into Eq. (114) yields the phenomenological relation for the internal-energy diffusive flux

$$\mathbf{J}_U = \sum_{i=1}^n h_i \mathbf{J}_{m_i} - \sum_{i=1}^n \frac{1}{\rho_i} \tilde{\mathbf{D}}_i^T \cdot \mathbf{x}_i - \lambda' \cdot \nabla T \quad (125)$$

In Eq. (125), the functional dependence ($-\mathbf{B}$) has been dropped from the transposed thermal-diffusion tensor in order to simplify the notation; nevertheless, this peculiarity should always be kept in mind.

In order to derive phenomenological relations analogous to Eqs. (122) and (125), several authors [23,35–37] followed an alternative procedure starting directly from Eq. (107). In their analyses, the term $v_i \nabla p_i$ appears as the *isothermal* gradient of the chemical potential whose definition descends from the following rearrangement

$$v_i \nabla p_i = \nabla \mu_i + \mathcal{S}_i \nabla T = \nabla \tau \mu_i \quad (126)$$

of Eq. (106). Then, the generalized forces associated with the component-mass diffusive fluxes in Eq. (107) appear as

$$\mathcal{F}_i = \nabla_T \mu_i + e N_A \frac{\sigma_{is}}{M_i} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (127)$$

The ensuing phenomenological relations for the component-mass diffusive fluxes and the internal-energy diffusive flux are further manipulated to bring forth the gradients of mass fractions (Fick law) and pressure. The drawback of this procedure resides in the fact that the intervening tensorial phenomenological coefficients, say \mathbf{L}'_{ij} , \mathbf{L}'_{it} , \mathbf{L}'_{Ti} , \mathbf{L}'_{TT} , are not expressible in terms of the kinetic-theory tensors \mathbf{D}_{ij} , \mathbf{D}_i^T , λ' as simply as in Eqs. (115)–(118) but, in order to obtain the required correlation, necessitate an elaborate manipulation involving the resolution of cumbersome algebraic systems of equations.

The phenomenological relations (122) and (125) are operational equations that, together with Eq. (111) and with adequate input from the kinetic theory, qualify to complement the set of governing equations in open form for the purpose of numerical calculations. However, noticeable insight towards the understanding of the transport processes can be gained if the role played by the contributions composing the generalized force \mathcal{X}_i is made explicit. The substitution of Eq. (111) into Eq. (122) yields

$$\mathbf{J}_{m_i} = \frac{\rho}{p} \frac{M_i}{M} \sum_{j=1}^n \frac{M_j}{M} \mathbf{D}_{ij} \cdot \nabla p_j + \mathbf{F}_i^m \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{1}{T} \mathbf{D}_i^T \cdot \nabla T \quad (128)$$

with the tensorial coefficients

$$\mathbf{F}_i^m = e N_A \frac{\rho}{p} \frac{M_i}{M^2} \sum_{j=1}^n \mathbf{D}_{ij} \rho_j \sigma_{js} \quad (129)$$

Equation (128) shows explicitly how the electromagnetic field participates to the build-up of the component-mass diffusive fluxes at the same footing of the partial-pressure and temperature gradients. The appearance of the mass-fraction gradients is one step away from Eq. (128) and is produced by expanding the partial pressures with the aid of the perfect-gas relations $p_i = x_i p$ and $x_i = \alpha_i M_i / M$. Accordingly, Eq. (128) becomes

$$\mathbf{J}_{m_i} = - \sum_{k=1}^{n-1} \mathbf{D}_{ik} \cdot \nabla \alpha_k + \mathbf{P}_i^m \cdot \nabla p + \mathbf{F}_i^m \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \frac{1}{T} \mathbf{D}_i^T \cdot \nabla T \quad (130)$$

with the tensorial coefficients

$$\mathbf{D}_{ik} = \left(\frac{M_i}{M_k} - \frac{M_i}{M_n} \right) \left(\sum_{j=1}^n \mathbf{D}_{ij} \rho_j \right) - \rho \frac{M_i}{M} (\mathbf{D}_{ik} - \mathbf{D}_{in}) \quad (131)$$

$$\mathbf{P}_i^m = \frac{1}{p} \frac{M_i}{M} \sum_{j=1}^n \mathbf{D}_{ij} \rho_j \quad (132)$$

Equation (130) warns against the uncareful practice of limiting the expressions of the component-mass diffusive fluxes to the sole Fick law, namely the first term on the right-hand side. Even in the event of negligible thermodiffusion and vanishing electromagnetic field, that widely assumed law may not be sufficient to characterize completely the component-mass diffusive fluxes because the tensorial coefficients \mathbf{P}_i^m , being constructed according to combinations of the diffusion tensors very similar to those that appear in Eq. (131), could have magnitudes comparable to the tensorial coefficients \mathbf{D}_{ik} . Thus, it seems safer not to discard *a priori* the pressure-gradient contribution in Eq. (130) but to let its negligibility, if any, arise spontaneously during the course of numerical simulations. Equation (131) illustrates the sometimes forgotten fact that the diffusion coefficients appearing in Fick law must be obtained *from appropriate adaptation* of those provided by the Chapman-Enskog method.

The substitution of Eq. (128) into Eq. (31) leads to a more explicit and meaningful expression of the conduction-current density

$$\mathbf{J}_Q = \sum_{j=1}^n \lambda_{ej}^p \cdot \nabla p_j + \lambda_e \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \lambda_e^T \cdot \nabla T \quad (133)$$

and to the recognition of the *pressoelectrical*-conductivity tensors

$$\lambda_{ej}^p = -e N_A \frac{\rho}{p} \frac{M_j}{M^2} \sum_{i=1}^n \sigma_{is} \mathbf{D}_{ij} \quad (134)$$

the electrical-conductivity tensor

$$\lambda_e = -(e N_A)^2 \frac{\rho}{p M^2} \sum_{i=1}^n \sum_{j=1}^n \sigma_{is} \mathbf{D}_{ij} \rho_j \sigma_{js} \quad (135)$$

in rigorous agreement with the expression derived by Chapman and Cowling [71], and the thermoelectrical-conductivity tensor

$$\lambda_e^T = e N_A \frac{1}{T} \sum_{i=1}^n \frac{\sigma_{is}}{M_i} \mathbf{D}_i^T \quad (136)$$

Equation (133) evidences unambiguously that the generalized Ohm law alone may not be sufficient to characterize the conduction-current density in an ionized gas

mixture because, even in the event of negligible thermodiffusion, the contributions associated with the partial-pressure gradients may not be negligible with respect to the diffusion promoted by the electromagnetic field. These considerations have a negative impact on the applicability of the magnetic-induction equation discussed in Sec. 5. At the same time, Eq. (135) casts skepticism about the physical meaningfulness of (actually, it severely admonishes against) undertaking flow-field simulations in the presence of the electromagnetic field in which the gas mixture is assimilated to a perfect gas without electrically charged carriers but still with a finite (scalar) electrical conductivity. This is a flagrant infringement of physical coherence because the electrically-conductivity tensor vanishes identically in the absence of electrically charged components, as Eq. (135) unconditionally indicates ($\sigma_{is} = \sigma_{js} = 0$).

An expression structured in the same style of Eq. (128) can be obtained also for the internal-energy diffusive flux by substituting Eqs. (111) and (128) into Eq. (125); the final outcome reads

$$\mathbf{J}_u = \sum_{j=1}^n \mathbf{P}_j^u \cdot \nabla p_j + \mathbf{F}^u \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \lambda_T^u \cdot \nabla T \quad (137)$$

with the tensorial coefficients

$$\mathbf{P}_j^u = \sum_{i=1}^n \left(\delta_{ij} \frac{1}{\rho_j} \tilde{\mathbf{D}}_j^T + \frac{\rho}{p} h_i \frac{M_i M_j}{M^2} \mathbf{D}_{ij} \right) \quad (138)$$

$$\mathbf{F}^u = e N_A \sum_{i=1}^n \left(\tilde{\mathbf{D}}_i^T \frac{\sigma_{is}}{M_i} + \frac{\rho}{p} h_i \frac{M_i}{M^2} \sum_{j=1}^n \mathbf{D}_{ij} \rho_j \sigma_{js} \right) \quad (139)$$

$$\lambda_T^u = \lambda' + \frac{1}{T} \sum_{i=1}^n h_i \mathbf{D}_i^T \quad (140)$$

There are two aspects related to Eq. (137), usually not encountered in traditional hypersonic-flow theory, that may have implications for spacecraft thermal protection during planetary reentry. As clearly shown in Eq. (137), there is a direct contribution arising just from the mere existence of the electromagnetic field. In particular, the influence of the magnetic induction disappears on the wall ($\mathbf{v} = 0$) of a reentry body but the influence of the electric field could still play a role. Moreover, Eq. (137) indicates also that, on the contrary of the widespread habitude acquired within the realm of a scalar transport theory, the component of \mathbf{J}_u normal to the wall of a reentry body depends not only on the normal gradients of partial pressures and temperature but also on their tangential gradients [23]. With the goal in mind of achieving a controlled mitigation of the internal-energy diffusive flux, this occurrence gives cause for the necessity to produce an accurate assessment of the importance of the off-diagonal terms in the transport tensors. More specifically,

a thorough understanding of the anisotropic character of the transport tensors under the influence of the electromagnetic field appears to be a worthwhile target. Chapman and Cowling [71] pioneered the study of this subject but the cases they considered were subdued to simplifications (steady states, slight or full ionization, binary mixtures, absence of chemical reactions, mixtures macroscopically at rest, and the like) which appear (sometimes very) restrictive when looked at from the perspective of hypersonics applications. Chapman and Cowling's findings and conclusions have reverberated throughout the literature [11,22,74]; unfortunately, the accompanying simplifications seem to have been somehow *diluted* during the reverberation process. Thus, central issues are still in demand of attention. For example, it is important to identify the circumstances according to which the anisotropy possessed by the transport tensors is or is not negligible, to recognize if the anisotropy works against or in favor of the sought mitigation, to investigate the existence of potential ways to enhance the anisotropy effects and drive them towards the sought mitigation. The work already done [71,74,75,77,82–90] requires improvement in the generality of the findings and, if necessary, in their adaptation to routine use in numerical calculations.

9.5 Scalar generalized forces

The derivation of the phenomenological relations relative to the scalar generalized forces is based on the entropy production related to the zero tensorial order

$$\dot{\mathcal{A}}_{v,0} = -\frac{1}{T}[-(\pi + p)]\nabla \cdot \mathbf{v} - \frac{1}{T} \sum_{k=1}^r \dot{\xi}_k \mathcal{A}_k \geq 0 \quad (141)$$

The application of the Curie postulate to Eq. (141) provides the phenomenological relations

$$-(\pi + p) = - \sum_{k=1}^r l_{vk} \mathcal{A}_k - l_{vv} \nabla \cdot \mathbf{v} \quad (142)$$

$$\dot{\xi}_k = - \sum_{j=1}^r l_{kj} \mathcal{A}_j - l_{kv} \nabla \cdot \mathbf{v} \quad (143)$$

The scalar phenomenological coefficients $l_{vk}, l_{vv}, l_{kj}, l_{kv}$ form an $[(r+1) \times (r+1)]$ matrix which must be positive definite in order to have the inequality (141) identically satisfied. Onsager reciprocal relations exist also for these coefficients; plenty of information is available in the specialized literature. The scalar phenomenological coefficients appearing in Eqs. (142) and (143) have not been investigated with the same attention devoted to the kinetic-theory tensors encountered in Secs. 9.3 and 9.4 because it was soon recognized [23,35,36,69] that the linear

combinations of the affinities in Eqs. (142) and (143) have very narrow limits of validity. The coefficient l_{vv} is better known as the bulk-viscosity coefficient

$$l_{vv} = \mu_v \quad (144)$$

and is the only one which has received attention because it characterizes the direct effect of the medium compressibility ($\nabla \cdot \mathbf{v}$) on the generation of normal stresses. Even with the limitation imposed by their restricted applicability, Eqs. (142) and (143) retain importance from a theoretical point of view because they reveal unambiguously the existence of cross effects between chemical reactions and medium compressibility [21,35–37]. This aspect has been systematically ignored by authors concerned with CFD applications. Notwithstanding a few daring attempts [91–93] towards theoretical progress on the subject matter, the concern expressed by Napolitano [35,36] in 1969 that

Not much is known nor is done ... to ascertain the order of magnitude of this type of coupling ...

is, unfortunately, still applicable today.

The disregard of cross effects brings Eq. (142) into the simplified form

$$\pi = -p + \mu_v \nabla \cdot \mathbf{v} \quad (145)$$

which finds widespread use in the applications, most often accompanied by the ulterior approximation of vanishing bulk viscosity ($\mu_v = 0$). In the same guise, Eq. (143) would become

$$\dot{\xi}_k = -l_{kk} \mathcal{A}_k \quad (146)$$

However, chemical-reactions rates are never used in the form (146) but, rather, in the non-linear form

$$\dot{\xi}_k = \kappa_k^f \prod_{i=1}^n \left(\frac{\rho_i}{M_i} \right)^{\nu_{ki}^{(r)}} - \kappa_k^b \prod_{i=1}^n \left(\frac{\rho_i}{M_i} \right)^{\nu_{ki}^{(p)}} \quad (147)$$

that features explicit dependence on the component partial densities and that sometimes is referred to as the law of mass action [23,35,36]. Equation (147) arises from a blend of theoretical considerations and (mainly) experimental evidence [76,94–99]. The reaction constants κ_k^f, κ_k^b are in reality functions of the temperature, customarily assumed in accordance with a modified version

$$\kappa^{f,b} = CT^\eta e^{-E_a/K_B T} \quad (148)$$

of the Arrhenius law, and are related to each other through the chemical-equilibrium constant defined in terms of the component concentrations

$$\frac{\kappa_k^f}{\kappa_k^b} = K_k^c(T) \quad (149)$$

A theoretical justification for Eq. (148) can be produced only in particularly simple cases. In it, K_B is the Boltzmann constant ($1.3806503 \cdot 10^{-23} \text{ J}\cdot\text{K}^{-1}$) while the constant C , the temperature exponent η , and the activation energy E_a are derived, in practice, by utilizing that expression as an interpolation formula constructed on experimentally determined data and, then, collected in databases [100,101] readily available to serve the needs of the applications. The reliability of Eq. (148) becomes weak in the high-temperature range due to serious difficulties encountered in carrying out accurate measurements. The uncertainties of the reaction constants at high temperatures is a well known and long standing problem in demand of resolution. In the chemical-equilibrium limit [$(A_k \rightarrow 0) \Rightarrow A_k/R_G T \ll 1$], Eq. (147) reduces [35–37,69] to Eq. (146) with the phenomenological coefficient given by

$$l_{kk} = \frac{\kappa_k^f}{R_G T} \prod_{i=1}^n \left(\frac{\rho_i^e}{M_i} \right)^{\nu_{ki}^{(r)}} = \frac{\kappa_k^b}{R_G T} \prod_{i=1}^n \left(\frac{\rho_i^e}{M_i} \right)^{\nu_{ki}^{(p)}} \quad (150)$$

The subscript “e” attached to the partial densities in Eq. (150) indicates chemical-equilibrium values corresponding to a local couple of thermodynamic parameters [(T, v) or (T, p)]; R_G is the universal gas constant ($8.314472 \text{ J}\cdot\text{K}^{-1}$).

Notwithstanding the widespread use of Eq. (147) in CFD, it is important to keep in mind that the premises on which it is constructed reflect the chemical kinetics of a perfect-gas mixture contained in a constant volume, macroscopically at rest, without spatial disuniformities, and whose population distributions over the quantum energy states associated with the molecular degrees of freedom can still be sufficiently assimilated to a Boltzmann distribution [35,36]. The chemical-kinetics phenomenology described by Eq. (147) is, therefore, substantially simpler than the more complex one accompanying hypersonics situations. For example, some unresolved, but of extreme relevance, issues are the failure of Eq. (147) to bring into account the influence of the medium compressibility, the intrinsic difficulty to adapt it to multitemperature situations, and its incompatibility with quantum-state populations that do not follow a Boltzmann distribution.

10 Conclusions

The understanding of the coupling between the hypersonic flow field of an ionized gas mixture and the electromagnetic field is conceptually straightforward in the ab-

sence of polarization and magnetization effects. The recognition of the weaknesses affecting the assumptions on which the derivation of the largely used magnetic-induction equation is based indicates that the adoption of either directly the Maxwell equations [Eqs. (36) and (37)] or the field equations for the electromagnetic scalar and vectorial potentials [Eqs. (44) and (45)] represents a better choice reflecting a more consistent physical description of the electromagnetic field. The cost to pay is the development of appropriate numerical algorithms that, especially in the case in which the field equations of the potentials are chosen, may turn out to be substantially different from those in use since many years in computational fluid dynamics. Obviously, the coverage of the physical phenomenology relative to polarization and magnetization is desirable for reasons of both scientific interest and engineering necessity. Thus, the open-form governing equations should be extended for that purpose. The extension should be accomplished in a bilateral manner, that is, not only by using the appropriate Maxwell equations but also by introducing the required ingredients on the fluid-dynamics side such as, for example, the specific angular momentum, its associated energy, their respective balance equations, and so on. Subsequently, the formalization of state-to-state thermal kinetics and radiation together with their integration in the open-form governing equations represent a wishful endeavour towards completion.

The open-form governing equations must be complemented with phenomenological relations. In this respect, the method of irreversible thermodynamics, based on the analysis of the entropy production, proves useful to recognize generalized fluxes and generalized forces at work in the flow, achieves deep insight into the physics of their cross couplings, and provides linear phenomenological relations that, although with the exception of the chemical-reaction rates, go rather far in satisfying the needs of engineering applications. The method straightforwardly reveals how the influence exerted by the electromagnetic field on the diffusion of (electrically-charged) component masses and internal energy becomes manifest. There is a novelty with respect to more habitual fluid-dynamics situations without electromagnetic field: the presence of the magnetic induction destroys the isotropy of the flow. The introduced anisotropy calls for particular attention to the possibility of cross coupling between generalized fluxes and forces of different tensorial order and to understand the importance of the tensorial nature of the transport coefficients with the goal in mind of exercising control over the distributions of internal-energy diffusive flux imposed on the surfaces of a body during planetary reentry. Multitemperature circumstances should not be underestimated. There have been efforts to bring the multitemperature phenomenology within the reach of irreversible thermodynamics but the actual status of the theory demands further improvements. This appears a mandatory task to pursue in order to incorporate correctly the effects originating from the thermal disequilibrium among the molecular degrees of freedom of the components.

The final goal of the theoretical fluid dynamicist is the construction of an adequate mathematical apparatus with the *proper* physics built in it. According to the

previous considerations, there is plenty of work in the theoretical arena awaiting investigation and understanding. New problems join old ones, some of which were identified and formulated long time ago but are still unresolved today. In this respect, it can be safely maintained that two antithetical approaches emerge. The *minimalist* approach consists in throwing into the equations a simplified physics, most of the times even stretched beyond its domain of applicability, and rushing to the computer in the hope that the discarded physics is unimportant and that either numerically predicted flows match experimental evidence within an acceptable approximation or sensitivity analyses produce conservative results. This is a risky approach. For one thing, accurate experimental evidence in hypersonic regime may be difficult to gather; in addition, the necessity imposed by engineering applications to produce results within awfully short time limits induces to yield at the temptation of *numerically* fine-tuning the physical models, an exercise that sometimes is camouflaged under the epithet of validation. The *maximalist* approach is characterized by an attitude of thoroughness towards the physics translated into the equations; conceptual difficulties are not avoided but are confronted without hesitation in order to push further ahead the comprehension of the phenomenology dealt with. This is a lengthy approach, certainly incompatible with the shortness of the time limits mentioned above. On the other hand, it is inescapable when the minimalist approach leads into a situation of stagnating failure. The choice between the two approaches is a matter of personal taste. The last years have seen an unquestionable unbalance towards the former approach sponsored by an unjustified rush to computational fluid dynamics. Probably, the most convenient way to go about is the one that takes advantage of both. When dealing with new physical complexities, the minimalist approach is acceptable to start with but resources should also be allocated to promote a parallel line of development following the maximalist-approach philosophy. In the author's opinion, the latter is a *sine qua non* condition to achieve progress in such a complex discipline as hypersonics is.

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Appendices

A Magnetic-induction equation

Neglecting the displacement-current density $\varepsilon_0 \partial \mathbf{E} / \partial t$, Eq. (37) becomes

$$\mathbf{j} = \varepsilon_0 c^2 \nabla \times \mathbf{B} \quad (\text{A.1})$$

Expanding the electric-current density in Eq. (A.1) according to Eq. (33) gives the conduction-current density

$$\mathbf{J}_Q = \varepsilon_0 c^2 \nabla \times \mathbf{B} - \rho_c \mathbf{v} \quad (\text{A.2})$$

The presumed applicability of the generalized Ohm law [Eq. (38)] brings Eq. (A.2) into the form

$$\lambda_e (\mathbf{E} + \mathbf{v} \times \mathbf{B}) = \varepsilon_0 c^2 \nabla \times \mathbf{B} - \rho_c \mathbf{v} \quad (\text{A.3})$$

from which the electric field

$$\mathbf{E} = \frac{\varepsilon_0 c^2}{\lambda_e} \nabla \times \mathbf{B} - \frac{\rho_c}{\lambda_e} \mathbf{v} - \mathbf{v} \times \mathbf{B} \quad (\text{A.4})$$

can be obtained. The substitution of Eq. (A.4) into Eq. (36) and the subsequent expansion of the terms affected by the curl operator leads to Eq. (40).

B Field equations for scalar and vector potentials

Taking into account that the divergence of a curl and the curl of a gradient give always a null result, Eq. (35) implies that the magnetic induction can be expressed in terms of a vector potential and of an arbitrary function of space and time as

$$\mathbf{B} = \nabla \times (\mathbf{A}' + \nabla \psi) \quad (\text{B.1})$$

The replacement of three scalar quantities, namely the components of the vector \mathbf{B} , with four scalar quantities, namely the components of the vector \mathbf{A}' and the scalar function ψ , introduces an arbitrariness about the vector potential $\mathbf{A} = \mathbf{A}' + \nabla \psi$

which, in order to be resolved, requires the assignment of a conveniently chosen scalar condition. With this provision, Eq. (B.1) can be simply rephrased as

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (\text{B.2})$$

The field equation for the vector potential derives from Eq. (37). Performing the curl on both sides of Eq. (B.2) yields

$$\nabla \times \mathbf{B} = \nabla \times (\nabla \times \mathbf{A}) = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} \quad (\text{B.3})$$

The substitution of Eq. (B.2) into Eq. (36) provides the form

$$\nabla \times \mathbf{E} + \frac{\partial}{\partial t} \nabla \times \mathbf{A} = 0 \quad (\text{B.4})$$

which, after permutation of the time derivative with the gradient operator, turns into

$$\nabla \times (\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t}) = 0 \quad (\text{B.5})$$

The quantity in brackets is, thus, irrotational and can be expressed as the gradient of a scalar potential

$$\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\nabla \phi \quad (\text{B.6})$$

From Eq. (B.6), the electric-field intensity is obtained in terms of the potentials as

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t} \quad (\text{B.7})$$

The substitution of Eqs. (B.3) and (B.7) into Eq. (37) leads to

$$\varepsilon_0 c^2 [\nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}] = \mathbf{j} - \varepsilon_0 \frac{\partial}{\partial t} (\nabla \phi + \frac{\partial \mathbf{A}}{\partial t}) \quad (\text{B.8})$$

which can be rearranged as

$$\frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla^2 \mathbf{A} + \nabla(\nabla \cdot \mathbf{A} + \frac{1}{c^2} \frac{\partial \phi}{\partial t}) = \frac{1}{\varepsilon_0 c^2} \mathbf{j} \quad (\text{B.9})$$

Inspection of Eq. (B.9) suggests that the gauge transformation

$$\frac{1}{c^2} \frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{A} = 0 \quad (\text{B.10})$$

rather than the gauge $\nabla \cdot \mathbf{A} = 0$, customarily imposed in magnetostatics, is the most convenient choice to resolve the arbitrariness about \mathbf{A} . The condition (B.10) is known as the Lorentz gauge [40,47]. Following it, Eq. (B.9) reduces to the simpler Eq. (45).

The field equation for the scalar potential derives from Eq. (34). The substitution of Eq. (B.7) into Eq. (34) gives

$$-\nabla \cdot (\nabla \phi) - \nabla \cdot \frac{\partial \mathbf{A}}{\partial t} = \frac{\rho_c}{\varepsilon_0} \quad (\text{B.11})$$

Equation (B.11) is equivalent to

$$-\nabla^2 \phi - \frac{\partial}{\partial t} \nabla \cdot \mathbf{A} = \frac{\rho_c}{\varepsilon_0} \quad (\text{B.12})$$

The term $\nabla \cdot \mathbf{A}$ is obtained from the Lorentz gauge [Eq. (B.10)]

$$\nabla \cdot \mathbf{A} = -\frac{1}{c^2} \frac{\partial \phi}{\partial t} \quad (\text{B.13})$$

and substituted into Eq. (B.12) to obtain Eq. (44).

C Transformation of the electromagnetic body force and derivation of the balance equation of electromagnetic momentum

The electric-charge density and the electric-current density can be obtained from Eqs. (34) and (37) as

$$\rho_c = \varepsilon_0 \nabla \cdot \mathbf{E} \quad (\text{C.1})$$

$$j = \varepsilon_0 c^2 \nabla \times \mathbf{B} - \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (\text{C.2})$$

and substituted into Eq. (49) to yield

$$\dot{\mathbf{g}}_v = \varepsilon_0 \mathbf{E} \nabla \cdot \mathbf{E} + \varepsilon_0 c^2 (\nabla \times \mathbf{B}) \times \mathbf{B} - \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \times \mathbf{B} \quad (\text{C.3})$$

At the same time, one can take advantage of Eqs. (35) and (36) to construct the identity

$$0 = \varepsilon_0 c^2 \mathbf{B} \nabla \cdot \mathbf{B} + \varepsilon_0 (\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t}) \times \mathbf{E} \quad (\text{C.4})$$

and to expand it into the expression

$$0 = \varepsilon_0 c^2 \mathbf{B} \nabla \cdot \mathbf{B} + \varepsilon_0 (\nabla \times \mathbf{E}) \times \mathbf{E} + \varepsilon_0 \frac{\partial \mathbf{B}}{\partial t} \times \mathbf{E} \quad (\text{C.5})$$

somewhat symmetrical with respect to Eq. (C.3). The sum of Eqs. (C.3) and (C.5) yields

$$\begin{aligned} \dot{\mathbf{g}}_v &= \varepsilon_0 c^2 [\mathbf{B} \nabla \cdot \mathbf{B} + (\nabla \times \mathbf{B}) \times \mathbf{B}] \\ &+ \varepsilon_0 [\mathbf{E} \nabla \cdot \mathbf{E} + (\nabla \times \mathbf{E}) \times \mathbf{E}] - \frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) \end{aligned} \quad (\text{C.6})$$

Taking into account that the terms in squared brackets can be contracted as

$$\mathbf{B} \nabla \cdot \mathbf{B} + (\nabla \times \mathbf{B}) \times \mathbf{B} = \nabla \cdot (\mathbf{B} \mathbf{B} - \frac{1}{2} B^2 \mathbf{U}) \quad (\text{C.7})$$

$$\mathbf{E} \nabla \cdot \mathbf{E} + (\nabla \times \mathbf{E}) \times \mathbf{E} = \nabla \cdot (\mathbf{E} \mathbf{E} - \frac{1}{2} E^2 \mathbf{U}) \quad (\text{C.8})$$

Eq. (C.6) can be rephrased in the final form

$$\dot{\mathbf{g}}_v = \nabla \cdot [\varepsilon_0 c^2 (\mathbf{B} \mathbf{B} - \frac{1}{2} B^2 \mathbf{U}) + \varepsilon_0 (\mathbf{E} \mathbf{E} - \frac{1}{2} E^2 \mathbf{U})] - \frac{\partial}{\partial t} (\varepsilon_0 \mathbf{E} \times \mathbf{B}) \quad (\text{C.9})$$

which, considering the definitions (49) and (51), coincides with Eq. (50).

D Transformation of the electromagnetic-energy production and derivation of the balance equation of electromagnetic energy

Equation (37) can be resolved to express the electric-current density as

$$\mathbf{j} = \varepsilon_0 c^2 \nabla \times \mathbf{B} - \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (\text{D.1})$$

Taking into account Eq. (D.1), the electromagnetic-energy production becomes

$$\mathbf{j} \cdot \mathbf{E} = \varepsilon_0 c^2 \mathbf{E} \cdot \nabla \times \mathbf{B} - \varepsilon_0 \mathbf{E} \cdot \frac{\partial \mathbf{E}}{\partial t} = \varepsilon_0 c^2 \mathbf{E} \cdot \nabla \times \mathbf{B} - \varepsilon_0 \frac{\partial E^2 / 2}{\partial t} \quad (\text{D.2})$$

The first term on the right-hand side of Eq. (D.2) can be easily transformed

$$\mathbf{E} \cdot \nabla \times \mathbf{B} = -\nabla \cdot (\mathbf{E} \times \mathbf{B}) + \mathbf{B} \cdot \nabla \times \mathbf{E} \quad (\text{D.3})$$

to bring forth the curl of the electric-field intensity. The substitution of Eq. (36) into Eq. (D.3) yields

$$\mathbf{E} \cdot \nabla \times \mathbf{B} = -\nabla \cdot (\mathbf{E} \times \mathbf{B}) - \mathbf{B} \cdot \frac{\partial \mathbf{B}}{\partial t} = -\nabla \cdot (\mathbf{E} \times \mathbf{B}) - \frac{\partial B^2/2}{\partial t} \quad (\text{D.4})$$

so that Eq. (D.2) finally takes the form

$$j \cdot \mathbf{E} = -\nabla \cdot (\varepsilon_0 c^2 \mathbf{E} \times \mathbf{B}) - \frac{\partial}{\partial t} \left[\frac{\varepsilon_0}{2} (E^2 + c^2 B^2) \right] \quad (\text{D.5})$$

that coincides with Eq. (72).

E Poynting-vector transformation

From Eqs. (73) and (74), the vector product between \mathbf{E}' and \mathbf{B}' can be expanded as follows

$$\begin{aligned} \mathbf{E}' \times \mathbf{B}' &= \mathbf{E} \times \mathbf{B} - \frac{1}{c^2} \mathbf{E} \times (\mathbf{v} \times \mathbf{E}) - \mathbf{B} \times (\mathbf{v} \times \mathbf{B}) \\ &\quad - \frac{1}{c^2} (\mathbf{v} \times \mathbf{B}) \times (\mathbf{v} \times \mathbf{E}) \end{aligned} \quad (\text{E.1})$$

The second term on the right-hand side of Eq. (E.1) expands as

$$\begin{aligned} \mathbf{E} \times (\mathbf{v} \times \mathbf{E}) &= (\mathbf{E} \cdot \mathbf{E}) \mathbf{v} - (\mathbf{E} \cdot \mathbf{v}) \mathbf{E} = (E^2 \mathbf{U} - \mathbf{E} \mathbf{E}) \cdot \mathbf{v} \\ &= \frac{E^2}{2} \mathbf{v} + \left(\frac{E^2}{2} \mathbf{U} - \mathbf{E} \mathbf{E} \right) \cdot \mathbf{v} \end{aligned} \quad (\text{E.2})$$

Similarly, the third term on the right-hand side of Eq. (E.1) expands into

$$\mathbf{B} \times (\mathbf{v} \times \mathbf{B}) = \frac{B^2}{2} \mathbf{v} + \left(\frac{B^2}{2} \mathbf{U} - \mathbf{B} \mathbf{B} \right) \cdot \mathbf{v} \quad (\text{E.3})$$

The fourth term on the right-hand side of Eq. (E.1) is a little bit more complicated. It expands as

$$\begin{aligned} (\mathbf{v} \times \mathbf{B}) \times (\mathbf{v} \times \mathbf{E}) &= (\mathbf{v} \times \mathbf{B}) \cdot \mathbf{E} \mathbf{v} = \mathbf{E} \cdot (\mathbf{v} \times \mathbf{B}) \mathbf{v} = \mathbf{v} \cdot (\mathbf{B} \times \mathbf{E}) \mathbf{v} \\ &= -\mathbf{v} \cdot (\mathbf{E} \times \mathbf{B}) \mathbf{v} \end{aligned} \quad (\text{E.4})$$

In the non-relativistic approximation, therefore, the term

$$\frac{1}{c^2}(\mathbf{v} \times \mathbf{B}) \times (\mathbf{v} \times \mathbf{E}) = -\frac{1}{c^2}\mathbf{v} \cdot (\mathbf{E} \times \mathbf{B})\mathbf{v} \quad (\text{E.5})$$

is negligible with respect to $\mathbf{E} \times \mathbf{B}$ and can be disregarded in Eq. (E.1). Taking into account the definition [Eq. (51)] of the Maxwell stress tensor, the substitution of Eqs. (E.2) and (E.3) into Eq. (E.1) and the subsequent multiplication by the factor $\varepsilon_0 c^2$ leads to Eq. (75).